A DICTIONARY

OF

APPLIED CHEMISTRY

VOL. IV.

A DICTIONARY OF APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

Assisted by Eminent Contributors

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OF

APPLIED CHEMISTRY

BY

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ASSISTED BY EMINENT CONTRIBUTORS

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ABBREVIATIONS
OF THE TITLES OF JOURNALS AND BOOKS.

Abbreviation	Full title
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Arch. Pharm.	Archiv der Pharmazie.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewers Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs-und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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OILSTONE. A fine-grained hone-stone used with oil for sharpening edged tools. The most celebrated is the Turkey oilstone, an extremely hard and compact material, obtained in the interior of Asia Minor, and exported from Smyrna. It contains 70–75 p.c. silica, 20–25 p.c. calcium carbonate, and a little alumina. Two varieties are recognised, the white and the black, the latter being slightly the harder. In this country the Charley Forest stone has obtained great repute as an oilstone for whetting tools and penknives. It is a fine-grained, silicious, slaty rock, worked at Whittle Hill in Charnwood Forest, Leicestershire. The Welsh oilstone is a somewhat similar material, from near Llyn Idwal in North Wales, whilst the Devonshire oilstones are obtained from the neighbourhood of Tavistock. Several kinds of oilstone are worked in the United States. The Arkansas stone is a compact or fine-grained rock of bluish-white colour, used for delicate instruments, like those of surgeons and watchmakers. Somewhat similar, but more abundant, is the Washita oilstone, a white, opaque stone used chiefly by carpenters, from the Washita (or Ouachita) River, Arkansas. The name 'novaculite' is also applied to the Arkansas and Washita stones. Their material consists almost entirely of chalcedonic silica (99·5 p.c.).

In preparing oilstones for use, the rough pieces are cut into regular shapes on the lapidary's wheel, fed with diamond powder, and are rubbed smooth with sand or emery on an iron plate. The slab of stone is in some cases cemented to a wooden base, by means of putty. Some of the stones are used not only for sharpening tools, but for finishing turned and planed surfaces of metal work. Oilstone powder is also employed for grinding the brass fittings of mathematical instruments (v. R. Knight, Trans. Soc. Arts, 50, 233; C. Holtzapffel, Turning, vol. 3, 1081; and G. P. Merrill, The Non-metallic Minerals, 2nd edit., 1910; v. also Whetstones).

F. W. R.

OKRA, also called gumbo; *Hibiscus esculentus* (Linn.), an annual plant bearing edible

pods. Zega (Chem. Zeit. 1900, 24, 871) found as the average of 4 analyses—

Water	Protein	Fat	N-free extract	Fibre	Ash
80·7	4·2	0·4	12·1	1·2	1·4

According to American analyses (Bull. 28, U.S. Dept. of Agric. 1899), the edible portion of the pods, used largely as a vegetable in America, is much more watery, as shown by the following figures :—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
90·2	1·6	0·2	4·0	3·4	0·6

whilst, according to the same authority, canned okra contains—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
94·4	0·7	0·1	2·9	0·7	1·2

(v. also Tinsley, Amer. Chem. J. 1893, 14, 625). H. I.

OLD FUSTIC is the wood of a tree known as the *Chlorophora tinctoria* (Gaudich), previously called *Morus tinctoria* (Linn.) which occurs wild in different tropical regions. The tree frequently grows to a height of over 60 feet, is exported in the form of logs, sawn straight at both ends, and usually deprived of the bark. The best qualities of old fustic come from Cuba and the poorer from Jamaica and Brazil. It is at the present time used very largely, and, together with logwood, is the most important of the natural dyestuffs.

The colouring matters of old fustic were first investigated by Chevreul (Leçons de chimie appliquée à la teinture, II. 150), who described two substances, one sparingly soluble in water, called *morin*, and a second somewhat more readily soluble. Wagner (J. pr. Chem. [i.] 51, 82) termed the latter *moritannic acid*, and considered that it possessed the same percentage composition as morin. Hlaziwetz and Pfaundler (Annalen, 127, 351), on the other hand, found that the so-called moritannic acid was not an acid, and as moreover its composition and properties were quite distinct from those of morin, they gave it the name 'Maclurin.'

Morin $C_{13}H_{10}O_7,2H_2O$. To isolate this colouring matter from old fustic a boiling extract

B

obtained in a similar way from quercetin pentamethyl ether.

Kostanecki, Lampe and Tambor (Ber. 1906, 39, 625) have synthesised morin by reactions similar to those found serviceable in the artificial preparation of fisetin and quercetin (see YOUNG FUSTIC and QUERCITRON BARK), but in this case the formation of the flavanone did not proceed smoothly and only a small quantity could be prepared. The synthesis is illustrated by the following formulæ—

2'-hydroxy-4':6':2:4-tetramethoxychalkone.

1:3:2':4'-tetramethoxyflavanone.

a-isonitroso-1:3:2':4'-tetramethoxyflavanone.

Morin trimethyl ether.

Morin.

Morin dyes mordanted woollen cloth shades which, though of a slightly stronger character, closely resemble those given by kaempferol.

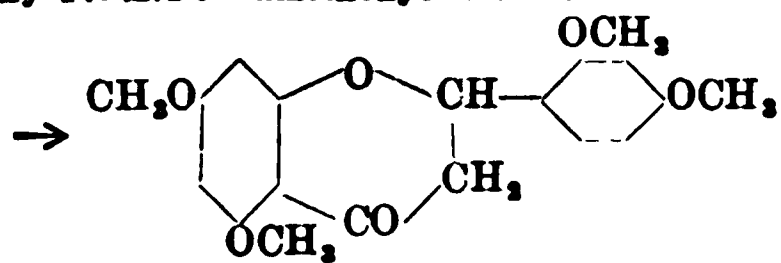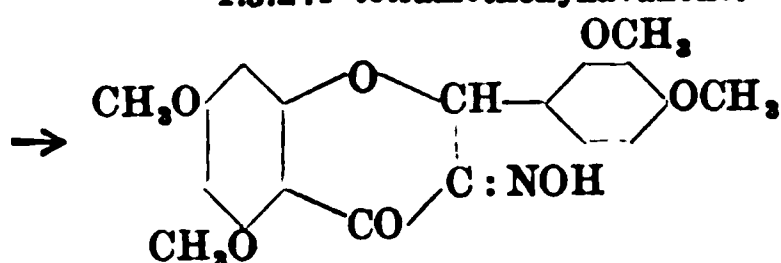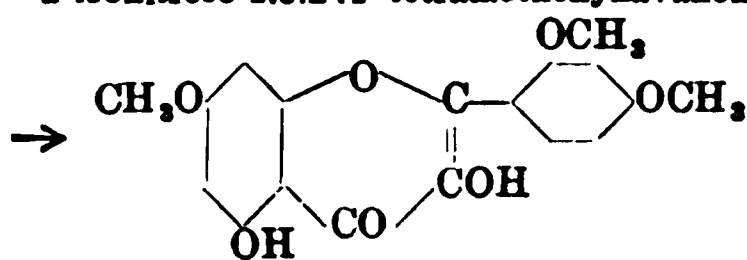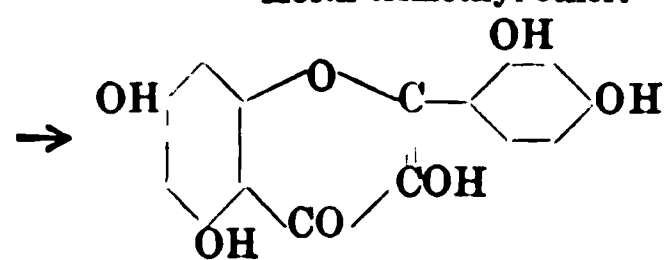|	Chromium	Aluminium	Tin	Iron
Morin	. Olive yellow	Yellow	Lemon yellow	Deep olive brown
Kæmpferol	Brown yellow	,,	Bright yellow	Deep olive brown

(Perkin and Wilkinson, Chem. Soc. Trans. 1902, 81, 590).

Maclurin $C_{13}H_{10}O_6$. When morin is precipitated from a hot aqueous extract of old fustic by means of lead acetate the solution contains maclurin. After removal of lead in the usual manner, the liquid is partially evaporated and extracted with ethyl acetate, which dissolves the colouring matter. The crude product is crystallised from dilute acetic acid (Perkin and Cope). A crude maclurin is also obtained during the preparation of fustic extract, partially in the form of its calcium salt, and this product is treated with dilute hydrochloric acid and crystallised from water. In order to decolourise the crystals, acetic acid is added to a hot aqueous solution and a little lead acetate in such quantity that no precipitate is formed,

and the solution is treated with sulphuretted hydrogen. The clear liquid is now much less strongly coloured, and after repeating the operation two or three times, the maclurin, which crystallises out on standing, possesses only a pale yellow tint.

When quite pure maclurin consists of colourless needles, m.p. 200° (Wagner, J. 1850, 529), somewhat soluble in boiling water, soluble in alkalis with a pale yellow colouration. With aqueous lead acetate it gives a yellow precipitate and with ferric chloride a greenish-black colouration.

Hlasiwetz and Pfaundler (J. 1864, 558) assigned the formula $C_{13}H_{10}O_6$ to maclurin, and found that by boiling with potassium hydroxide solution it gives phloroglucinol and protocatechuic acid.

Pentabenzoylmaclurin $C_{13}H_5O_6(C_7H_5O)_5$ melts at 155°-156° (König and Kostanecki, Ber. 1894, 27, 1996); and tribrom maclurin

$$C_{13}H_7Br_3O_6,H_2O,$$

colourless needles has been obtained by Benedikt. Maclurin pentamethyl ether $C_{13}H_5O(OCH_3)_5$, colourless leaflets, melts at 157°. König and Kostanecki first assigned to maclurin the constitution of a pentahydroxybenzophenone—

W. H. Perkin and Robinson (Chem. Soc. Proc. 1906, 22, 305), and somewhat later Kostanecki and Tambor (Ber. 1906, 39, 4022) synthesised maclurin pentamethyl ether, by the interaction of veratric acid and phloroglucinol trimethyl ether in presence of aluminium chloride—

Pentamethylmaclurin.

When maclurin pentamethyl ether is digested with alcoholic potash and zinc-dust leucomaclurin-pentamethyl ether (Kostanecki and Lampe, Ber. 1906, 39, 4014)

is produced in prismatic needles, m.p. 109°-110°, and this on further reduction gives pentamethoxydiphenyl methane, m.p. 107°-108°.

On the other hand, if leucomaclurin pentamethyl ether is oxidised in acetic acid solution, veratric acid and dimethoxybenzoquinone are formed.

Maclurin is interesting as it represents the only simple benzophenone colouring matter which is as yet known to exist in nature. It is possible, however, that kinoin from Malabar kino, and aromadendrin from eucalyptus kino also belong to this class (v. KINO).

Patent fustin. Under the name of 'patent fustin' a colouring matter has been placed on

the alkaline metals in calico-printing has been noted under article ANTIMONY, vol. i. The normal salt $Sb_2O_3 \cdot C_4O_4 2H_2O$ is obtainable by boiling antimonious chloride or oxychloride in oxalic acid, or by mixing a saturated solution of oxalic acid with a hydrochloric acid solution of the trichloride. It crystallises out as a granular precipitate. The antimony potassium oxalate $SbK_3(C_2O_4)_3 6H_2O$ is obtained in monoclinic crystals from a solution of antimonic acid in acid potassium oxalate. It is used as a mordant in dyeing. The sodium salt $SbNa_4(C_2O_4)_4 10H_2O$ is similarly prepared.

Cerium oxalate $Ce_2(C_2O_4)_3 10H_2O$ is a white, slightly granular, insoluble powder, permanent in the air, odourless and tasteless. It may be prepared by the action of oxalic acid solution on cerous oxide, or by addition of oxalic acid to a soluble cerium salt. Cerium oxalate has medicinal properties resembling those of bismuth subnitrate, and is used to prevent the vomiting of pregnancy and in certain diseases (Jolin, Bull. Soc. chim. [ii.] 21, 540).

Methyl oxalate $C_2O_4(CH_3)_2$ is obtained in rhombic tables melting at 54° and boiling at 163° by dissolving anhydrous oxalic acid in methyl alcohol and washing the crystals with cold water. Methyl oxalate is converted into oxalic acid and methyl alcohol by boiling with water. Pure oxalic acid may thus be prepared (v. METHYL).

Ethyl oxalate $C_2O_4(C_2H_5)_2$ is a liquid which may be obtained by slowly heating a mixture of 3 parts of the anhydrous acid and 2 parts of absolute alcohol to 100°, afterwards heating to 125° or 130° while the vapour of 2 parts of absolute alcohol is passed in. The ethyl oxalate is separated by fractional distillation. This compound is an aromatic oily liquid boiling at 186° and decomposed by water in the same manner as methyl oxalate.

A great number of aromatic esters of oxalic acid have been prepared and characterised by Bischoff and Hedenström (Ber. 1902, 3437); and also by Anselmino (Ber. Deutsch. Pharm. Ges. 1903, 494).

The decomposition of oxalates on heating, though taking place approximately according to the equation $CaC_2O_4 = CaCO_3 + CO$ in the case of calcium oxalate is in reality more complex. Some carbon is always produced during the ignition of calcium oxalate. Sodium and barium oxalates follow the courses $7Na_2C_2O_4 = 7Na_2CO_3 + 3CO + 2CO_2 + 2C$ and $8BaC_2O_4 = 8BaCO_3 + 6CO + CO_2 + C$. Magnesium oxalate gives equal volumes of CO and CO_2 and no carbon, $MgC_2O_4 = MgO + CO + CO_2$; but most other oxalates give notable quantities of carbon dioxide and carbon (Scott, Chem. Soc. Proc. 1904, 156).

The electrolytic reduction of oxalic acid and oxalates in sulphuric acid solution to derivatives of glyoxylic acid was first patented by Portheim (U.S. Pat. 798920, 1905).
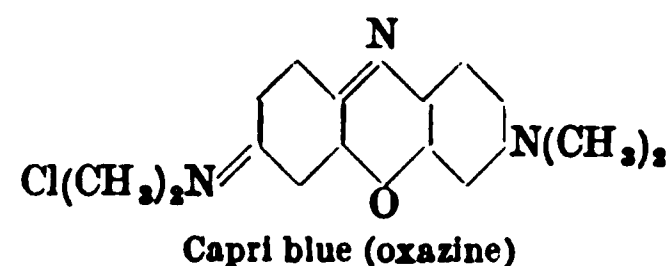
Kinzlberger and Co. (D. R. P. 163842) reduce oxalic acid, its esters, and amide electrolytically in a cell with a lead cathode and a diaphragm in presence of sulphuric acid of strengths varying from 2 to 90 p.c. monohydrate. The current density is 2 to 10 amps. per sq. cm. and the temperature must be kept low. Oxanilic acid or its derivatives in the same conditions yield phenylglycine or a derivative (v. also U.S. Pat.

837083; D. R. PP. 204787, 194038). Kinzlberger & Co. have since secured an additional patent for the use of electrodes of metals not attacked by sulphuric acid, particularly mercury (D. R. P. 210693). Bayer & Co. make use of sodium amalgam in the reduction of oxalic acid derivatives (D. R. P. 201895; J. Soc. Chem. Ind. 1908, 1176).

OXALIC ACID FERMENTATION v. FERMENTATION.

OXAMINE BLUE, -MAROON, -RED, -VIOLET v. AZO- COLOURING MATTERS.

OXAZINE COLOURING MATTERS.—The colouring matters of this series are closely related in structure to those of the thiazine group, the only difference in their general formulæ being caused by the replacement of the coupling sulphur atom by oxygen. Two typical examples in Capri blue and methylene blue will illustrate this statement

Methylene blue (thiazine)

Capri blue (oxazine)

Constitution.—The formula for Capri blue given above represents this substance as a derivative of p-quinone-diimide in which salt formation is produced on the imido nitrogen as in, for example, magenta. Within recent years, attempts have been made to assign to the oxazines an ortho-quinone formula of the same character as that which is now generally accepted as best expressing the structure of the colouring matters of the azine series. On this basis the formula of Capri blue becomes

in which salt formation is represented as having taken place through the passage of diad into tetrad oxygen. The work of Kehrmann and others shows that many of the properties of these compounds can be better explained by the oxonium formula than by the para-quinone structure. In the present article the oxonium formulæ have been used mainly for the sake of uniformity, although it must be remembered that it is by no means certain that the para-quinone structure of the salt is incorrect.

General description and methods of preparation.—The colouring matters of the series may be conveniently classed under two heads : (a) the basic colours ; (b) the mordant colours.

(a) *The basic colours.*—These compounds are the hydrochlorides, sulphates, and, in some cases, the zinc chloride double salts of the oxazines

bases. The most typical member is **Meldola's blue**, which was prepared by Meldola in 1879 and was the first colour of the series to be isolated. In the first instance the preparation was effected by allowing β-naphthol to react with nitrosodimethylaniline hydrochloride in glacial acetic acid solution. At the present time alcohol is used as a solvent and the colour is obtained by the following means.

Preparation.—A mixture containing 21 grams of β-naphthol and 53 grams of nitrosodimethylaniline hydrochloride is dissolved in alcohol and boiled for one day in a flask fitted with a reflux condenser. The colouring matter is formed in solution and is isolated as the zinc chloride double salt by adding a solution of zinc chloride until no further precipitate is obtained. The yield is 30 grams.

Properties.—The colour is a dark violet powder, soluble in water forming a bluish-violet solution. It dyes cotton mordanted with tannic acid and tartar emetic an indigo shade of blue.

Mechanism of formation.—There is no doubt that the formation of an oxazine colouring matter, in the manner described above, involves the reduction of one-third of the nitrosodimethylaniline used to *asym*-dimethyl-*p*-phenylenediamine and that the equation representing the formation of Meldola's blue can be written as follows :—

It is advisable, however, to use a larger quantity of nitrosodimethylaniline than is indicated in the above equation and to employ two molecules of the aniline derivative to one of the naphthol in all reactions of this type.

Literature.—Meldola (Ber. 1879, 12, 2065 ; Chem. Soc. Trans. 1881, 39, 37) ; Nietzki and Otto (Ber. 1888, 21, 1745) ; Witt (*ibid.* 1890, 23, 2247) ; Nietzki and Bossi (*ibid.* 1892, 25, 2994). Meldola's blue appears in commerce under other names of which the following are the more important : new blue, naphthylene blue, fast blue, cotton blue, fast navy blue and naphthol blue.
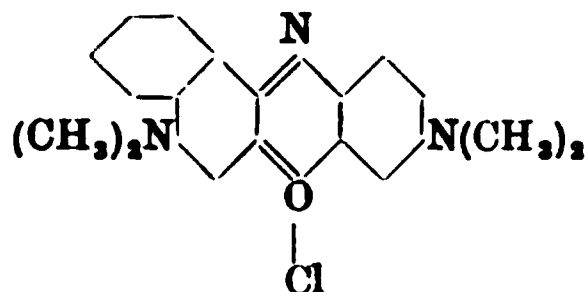
It is evident from the above equation that the formation of an oxazine colouring matter of the type of Meldola's blue might be expected to ensue when any derivative of β-naphthol is treated with a derivative of nitrosodimethylaniline provided that in the one case the adjacent position to the hydroxyl group is unoccupied

and in the other the ortho- position to the nitroso group is free. In practice, however, the formation of colours of this character is confined to the simpler reaction. Nevertheless, a new method for the preparation of these colours was introduced by Reissig in 1888, and by its means a number of important colours were added to the group. The new process can be best illustrated by referring to the production of **Nile blue A**, which is produced by the interaction of nitrosodiethyl-*m*-aminophenol hydrochloride and α-naphthylamine.

Preparation.—A quarter litre flask, fitted with an air condenser, containing 10 grams of α-naphthylamine hydrochloride dissolved in 100 grams of glacial acetic acid containing 20 p.c. of water, is heated on the sand bath until the contents are at the boiling-point when 19 grams of nitrosodiethyl-*m*-aminophenol hydrochloride are added in small portions at a time. The vigorous reaction which is caused by each addition is allowed to subside before a fresh portion is added. When all the phenol has been used the mixture is allowed to boil for half an hour when the colouring matter separates as glistening crystals on cooling.

Properties.—Crystalline powder, with marked bronze reflex, soluble in water, alcohol or pyridine forming a blue solution. Dissolves in concentrated sulphuric acid forming an orange-red solution which, on dilution, passes through green to blue. It is employed for the dyeing of tannined cotton on which it produces a bright shade of blue.

Mechanism of formation.—The production of Nile blue A may be expressed by an equation similar to that given in the case of Meldola's blue, as shown below :

Literature.—Reissig (B. A. S. F.), E. P. 4476, 88 ; 11046, 91 ; Am. P. 431541, 90 ; D. R. P. 45268, 88 ; 74391, 91 ; F. P. 189359, 88 ; Bayer, D. R. P. 49844, 89 ; F. P. 198589 ; Möhlau and Ullmann (Annalen, 289, 111) ; Thorpe (Chem. Soc. Trans. 1907, 91, 324). The commercial product is usually the sulphate.

Other members of class (*a*) may be summarised as under ; they are employed as tannin cotton colours.

Capri blue is formed from nitrosodimethylaniline and diethyl-*m*-aminocresol (Bender, 1890), and the **Cresyl blues** (Bender, 1892) are derived from nitrosodialkyl-*m*-amino-*p*-cresol and meta- or para-diamines.

New blue R is formed by the condensation of

asym-dimethyl-p-phenylenediamine with Meldola's blue.

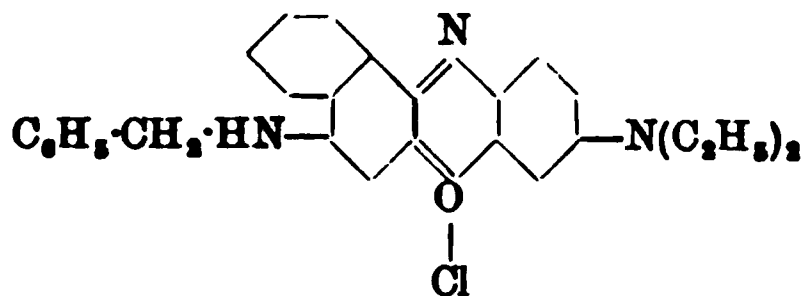$(CH_3)_2N \cdot C_6H_4 \cdot HN$ —$N(CH_3)_2$

It has been already stated that this base is a by-product in the formation of Meldola's blue. It therefore follows that New blue is always present in small quantities in commercial Meldola's blue.

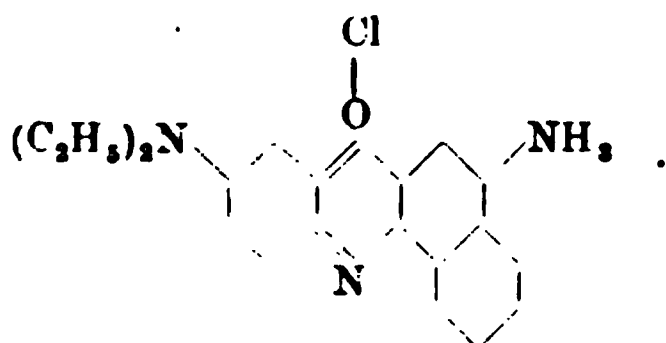**New methylene blue** is formed by the action of dimethylamine on Meldola's blue.

$(CH_3)_2N$ —$N(CH_3)_2$

It dyes cotton mordanted with tannin a greenish-blue, fast to light and washing and is also employed for the dyeing of silk.

Nile blue 2B is formed by the condensation of nitrosodiethyl-m-aminophenol hydrochloride and benzyl-a-naphthylamine (P. Julius, 1891)

$C_6H_5 \cdot CH_2 \cdot HN$ —$N(C_2H_5)_2$

The basic colours of this series have been used for some considerable time as stains for the purpose of colouring microscope sections; like other basic colours, they stain the nitrogenous parts of the section leaving the neutral regions uncoloured. It has been shown by Lorrain Smith (J. Path. Bact. 1907, 12, 1) that certain colours of the oxazine series possess the curious property of staining sections containing nitrogenous matter and neutral fat differentially; that is to say, whilst the nitrogenous matter is coloured blue in the usual manner the neutral fat is stained red. The colouring matter which exhibits this property to the greatest degree is Nile blue A, and there is no doubt that the cause of this behaviour is due to the partial hydrolysis of the dye in solution, thus—

$(C_2H_5)_2N$ —NH_2

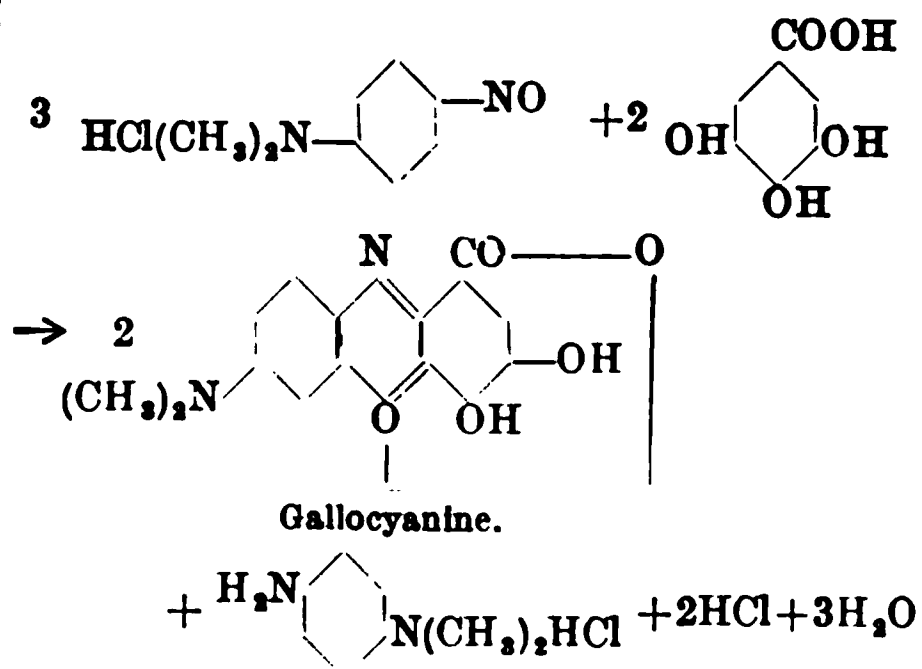**Nile blue A (chloride).—Blue.**

$(C_2H_5)_2N$ —O

The phenonaphthoxazone.—Red.

It is found (Chem. Soc. Trans. 1907, 91, 324) that small quantities of the oxazine are formed so soon as the dye is dissolved in water and that it is readily extracted by neutral solvents. It is evident, therefore, that the staining of the neutral fat is due to the extraction of the oxazine by the fat.

(b) *The mordant colours.*—The colouring matters of this section are prepared by the condensation of nitrosodialkylanilines with compounds of the type of gallic acid. The oxazine contains, therefore, two hydroxyl groups in the ortho- position to the coupling oxygen atom; consequently, like alizarin, they yield insoluble lakes with metallic salts and can be employed as mordant colours. A typical member of this group is **Gallocyanine**, which can be prepared by the condensation of nitroso-dimethylaniline with gallic acid.

Preparation.—A mixture of 10 grams of gallic acid and 17 grams of nitrosodimethyl-aniline hydrochloride is dissolved in 200 c.c. of alcohol (95 p.c.) contained in a 500 c.c. round-flask which is fitted with a reflux condenser. The reaction is completed by heating on the water-bath until a drop, removed by the aid of a glass rod, shows a deep violet spot, without a yellow rim, when placed on filter paper. The alcohol is then distilled off on the water-bath, and the dried residue, after being boiled with 200 c.c. of water and separated by filtration, is dried on porous porcelain. The colouring matter is a bronze powder insoluble in water. It dyes chrome-mordanted wool bluish-violet, and is also used for printing upon chrome-mordanted wool and cotton.

Mechanism of formation.—The course of the reaction, which is of the same character as that already shown, can be illustrated by the following equation—

$3 \; HCl(CH_3)_2N$ —NO $+2$ OH —$COOH$, OH, OH

$\rightarrow 2 \; (CH_3)_2N$ —$N \; CO$ —O, OH, OH

Gallocyanine.

$+ H_2N$ —$N(CH_3)_2HCl$ $+2HCl+3H_2O$

Literature.—H. Köchlin, D. R. P. 19580,1881; E. P. 4899, 1881; Am. P. 253721, 257498; Mon. Scien. 1883 (3) 13, 292; Nietzki and Otto (Ber. 1888, 21, 1736; 1892, 25, 2994).

The other dyestuffs of this group are, for the most part, derived either directly from gallocyanine by the action of various reagents, or by processes in which gallic acid or a derivative of this substance is employed. The following are the more important members.

Delphine blue (Hagenbuch, 1889) is prepared by sulphonating the product formed by the action of gallocyanine hydrochloride on aniline. The **Chromocyanines** (de la Harpe and Vaucher,
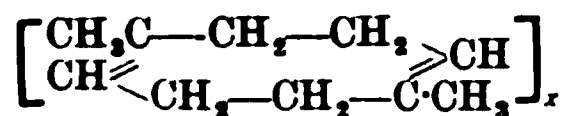
D

it yields a *superperozonide* $C_{18}H_{34}O_7$, possibly $CH_3[CH_2]_7CH\cdot CH\cdot[CH_2]_7\cdot CO_3H$

$\diagdown O_4\diagup$

, which is a colourless substance, not much more explosive than the other ozonides and has the same general chemical properties.

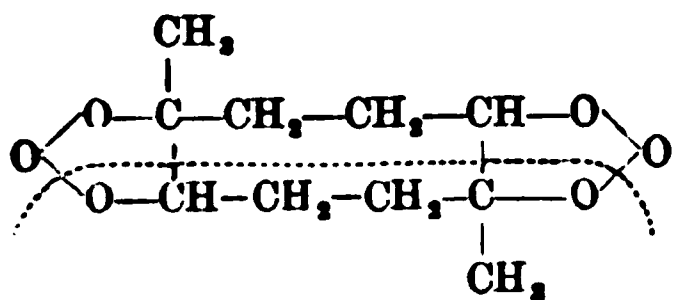Elaidic acid yields a normal and a perozonide which seems to differ little if at all from those of oleic acid.

Citronellic acid yields a similar ozonide, per- and superperozonide (Harries and Himmelmann, Ber. 1908, 41, 2187).

Cholesterol ozonide $C_{27}H_{46}O_5$, which is probably an oxozone derivative, forms a very stable white powder and, when boiled with water, yields hydrogen peroxide, aldehydes and much resinous products. Similar ozonides of cholesterol derivatives have also been obtained (Diels, Ber. 1908, 41, 2596; Langheld, *ibid.* 1023).

The most interesting application of the formation of ozonides to the elucidation of the structure of a compound is perhaps that of rubber. When the latter is treated with 5·5–6 p.c. of ozone, in chloroform solution for one hour for every gram, and the product evaporated *in vacuo* below 20° and the residue purified in the usual way, a *diozonide* $C_{10}H_{16}O_6$ is formed as a yellow thick oil. It dissolves in various solvents yielding, not colloidal, but ordinary solutions, and when boiled with water or distilled with steam it yields lævulic aldehyde and acid, and lævulic aldehyde superoxide. The formation of this ozonide and its decomposition products, together with the fact that when heated, rubber yields, amongst other products, *iso*prene and dipentene, has led Harries to give the following formula to rubber

$$\begin{bmatrix} CH_3C\text{—}CH_2\text{—}CH_2 \diagdown CH \\ CH \diagdown CH_2\text{—}CH_2\text{—}C\cdot CH_3 \end{bmatrix}_x$$

which agrees very well with its other known reactions. With ozone, it would form the di-ozonide

CH_3
|

which, on decomposing, breaks at the dotted lines and therefore yields

$O:O:C(CH_3)\cdot CH_2\cdot CH_2\cdot CH:O:O$

$+ OCH\cdot CH_2\cdot CH_2COCH_3$

Lævulic aldehyde diperoxide is readily transformed to the aldehyde in the presence of steam, consequently the lævulic aldehyde is present in large quantity (Harries, Ber. 1905, 38, 1195).
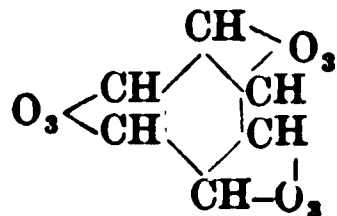
Gutta-percha gives a diozonide which seems identical with rubber diozonide, but on decomposition with water, it yields much less aldehyde and more acid : its decomposition has therefore been represented as taking place chiefly thus

CH_3
|

yielding

$OC(CH_3)\cdot CH_2\cdot CH_2\cdot CH:O:O + O:OCH\cdot CH_2\cdot CH_2\cdot C\diagup{O}\diagdown{CH}$

the latter readily being transformed into acid. The difference in behaviour of the two ozonides on decomposition is assumed to be due to some form of stereo-isomerism (*ibid.* 3985).
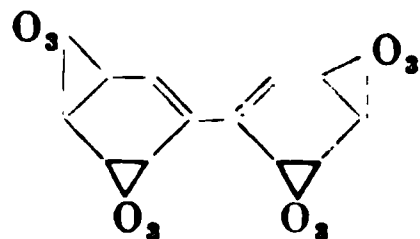
Benzene triozonide or ozobenzene

is formed by passing absolutely dry 5 p.c. ozone into dry benzene at 5°–10° for about 2 hours. It is stable in dry air at the ordinary temperature and forms a white amorphous mass which, if quite pure, becomes crystalline when treated with water at 0°. It is soluble in acetic acid but not in other organic solvents. When warmed quickly it explodes violently, and when treated with water it yields chiefly glyoxal $OHC\cdot CHO$ and some glyoxylic acid which probably results from the oxidation of the aldehyde with the hydrogen peroxide formed in the first reaction. These reactions show almost conclusively that benzene has three double linkings and that Kekulé's structural formula for benzene is correct.
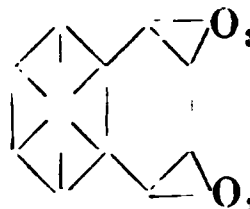
Only the decomposition products of the triozonides of toluene *o*- and *m*-xylene and of mesitylene have been obtained.

Diphenyl forms a *tetraozonide*

obtained as a crystalline mass, which explodes violently when heated. The fact that two more ozone molecules are not added at the double linkings is probably due to steric hindrance.

Naphthalene, when strongly cooled and submitted to the action of ozone, yields a crystalline

diozonide, thus , indicating that, in

all probability, only one of the rings has the benzene or Kekulé structure, whilst the other, possibly, has the concentric form. When treated with water the diozonide yields phthalic aldehyde $C_6H_4(CHO)_2$, phthalic acid, glyoxal, and glyoxylic acid.

Phenanthrene when treated similarly also forms a diozonide $C_{14}H_{10}O_6$ having similar properties to the naphthalene diozonide.

Tetrahydrobenzeneozonide $C_6H_{10}O_3$, obtained by passing ozone into a chloroform solution of

In either case the metal must be heated in hydrogen and then cooled in carbon dioxide.

Literature.—Bunsen, Phil. Mag. 1868, [iv.] 36, 253; Philipp, Dingl. Poly. J. 1876, 220, 95; Guyard, Compt. rend. 1863, 56, 1177; Leidie, *ibid.* 1900, 131, 888; Orloff, Chem. Zeit. 1906, 30, 714.

Palladium is a silver-white metal as hard as platinum but less ductile. It has a sp.gr. of 11·97 (Violle) and melts at 1546° (Waidner and Burgess, J. Soc. Chem. Ind. 1907, 1140). When heated to low redness in air, it becomes bluish, but it regains its white appearance at higher temperatures. At the melting-point of iridium, it boils and volatilises as a green vapour with partial oxidation.

It unites with fluorine and chlorine at a dull red heat, and superficially with iodine when treated with alcoholic iodine solution. Palladium is readily attacked by *aqua regia*, but less so by other acids. It unites with sulphur and selenium, less readily with phosphorus and arsenic, and with silicon at a white heat. It forms alloys with many metals.

Palladium has been employed for the graduated circles, &c., of philosophical instruments, and, to a small extent, in watch-making, and has been used for the electro-plating of parabolic mirrors on account of its silvery appearance and absence of change on exposure to impure air. It is also used for soldering platinum, but the bulk of the output is employed in the manufacture of dental alloys.

Palladium, in the form of palladium asbestos, is said to give excellent results when used as a contact substance in combustion analyses. It may be prepared for this purpose by precipitating a solution of pure palladium chloride in the presence of asbestos, by means of alkaline sodium formate (Jacobsen and Landesen, Ber. 1907, 40, 3217; Dennstadt, *ibid.* 3677).

Palladium, either in the form of sponge or black, has catalytic properties in a greater degree than platinum.

Literature on the catalytic properties of palladium and of colloidal palladium, Coquillon, Compt. rend. 1878, 87, 795; Phillips, Zeitsch. anorg. Chem. 1894, 6, 213; Lunge and Akunoff, *ibid.* 1900, 24, 191; Kraut, Ber. 1887, 20, 1113; Jahn, *ibid.* 1889, 22, 989; Zelinsky, *ibid.* 1898, 31, 3203; Bredig and Fortner, *ibid.* 1904, 3, 798; Paal and Roth, *ibid.* 1908, 41, 2273, 2282; *ibid.* 1909, 42, 1553; *ibid.* 1910, 43, 2684, 2692.

Palladium sponge or black would be employed on a commercial scale instead of or in conjunction with platinum if a sufficient supply were available.

Palladium absorbs various gases in quantities varying with its physical state (Cailletet and Collardeau, Compt. rend. 1894, 119, 830; Mond, Ramsay and Shields, Proc. Roy. Soc. 1897, 62, 290; Harbeck and Lunge, Zeitsch. anorg. Chem. 1898, 16, 50).

At ordinary temperatures, a palladium wire will absorb between 300 and 400 times its bulk of hydrogen and, when heated to redness in hydrogen, it absorbs nearly 1000 volumes and increases in bulk by nearly 10 p.c. This 'alloy' of hydrogen and palladium is permanent in air and *in vacuô* at ordinary temperatures, but yields up the whole of its hydrogen when

heated *in vacuô* (Mond, Ramsay and Shields, Chem. News, 1897, 76, 317; Dewar, *ibid.* 274; Fischer, J. Soc. Chem. Ind. 1906, 993).

'Palladium hydrogen' is a valuable reducing agent (Sabatier and Senderens, Compt. rend. 1892, 114, 1430; Ann. Chim. Phys. 1896, 7, 357, 383; Engel, Compt. rend. 1899, 129, 518; Keiser, Ber. 1887, 20, 2323).

In presence of water and of oxygen, palladium hydrogen seems to behave as an oxidising agent, this being probably due to the formation of hydrogen peroxide, which in the presence of palladium, behaves as the oxidiser (Traube, Ber. 1889, 22, 1496; Hoppe-Seyler, *ibid.* 2215).

The salts of palladium have so far been but little applied to technical use, but some of them, like potassium palladium chloride, are employed for toning in photography (J. Soc. Chem. Ind. 1911, 1410). The metal is commonly included in the sub-group which includes the metals rhodium and ruthenium. All three are lighter, melt more readily and are more easily volatilised, oxidised, and dissolved than the other metals of the platinum group. The division of the platinum metals into two groups is, however, somewhat arbitrary, and depends mainly on difference in density; and palladium, like osmium, would almost require to be placed alone except as regards this one point, if subdivision were permissible.
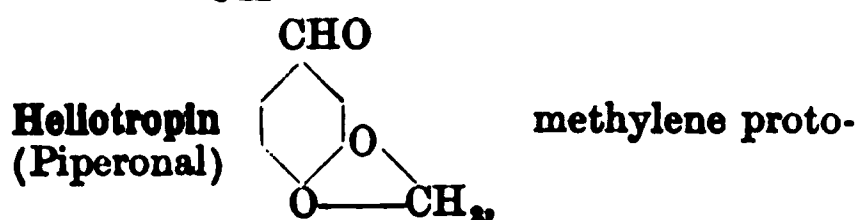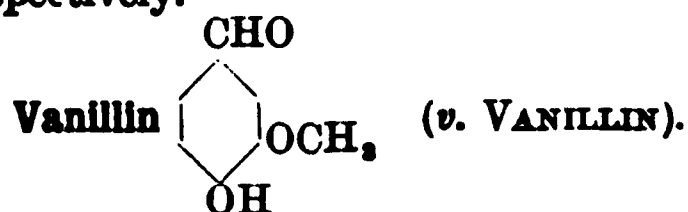
PALLADIUM COMPOUNDS.

Oxides. **Palladium monoxide** PdO may be prepared as an amber-coloured mass, yielding a black powder, by heating a mixture of a palladium salt with potassium carbonate; or as a bluish-green mass by heating the spongy metal in a current of oxygen at 700°–840°. It acts as a powerful oxidising agent to organic substances, and is reduced to metal by hydrogen or hydrogen peroxide. When freshly precipitated in the cold from a palladous salt with sodium carbonate, the *hydroxide* is dark brown, and is readily soluble in alkalis. If dried or precipitated from a boiling solution it becomes insoluble. The *palladious* salts which correspond to this oxide, are of a green, red, or brown colour, and have an astringent taste.

Palladium dioxide PdO_2 may be obtained in an impure hydrated form, soluble in acid, by the interaction of caustic soda and a palladichloride, or in a purer form, by the anodic oxidation of the nitrate (Wöhler and König, Zeitsch. anorg. Chem. 1905, 46, 323; *ibid.* 1906, 48, 203). It is a vigorous oxidising agent.
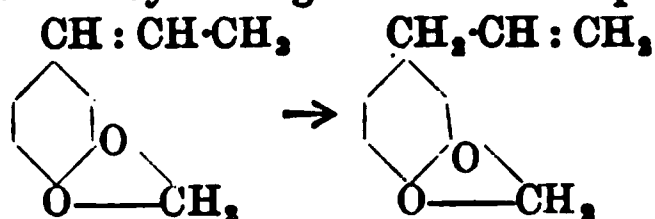
Palladium sesquioxide Pd_2O_3 is best prepared by the electrolytic oxidation of a concentrated solution of palladious nitrate at 8° with a current density of 0·5 cm. amp./cm²; but if the electrolysis is prolonged, the dioxide is formed (Wöhler and Martin, *ibid.* 1908, 57, 398). It forms a dark brown unstable powder; gives unstable solutions in hydrochloric acid, and when suspended in ether and mixed with alkali chlorides, on addition of hydrochloric acid, the double chlorides $PdCl_3,2MCl$ are formed, which in contact with water yield the salts M_2PdCl_4.

Halogen compounds. **Palladious chloride** $PdCl_2$ may be prepared by the action of air or of chlorine and hydrochloric acid on the metal, or by heating palladious sulphide in dry chlorine (Matignon, Compt. rend. 1903, 137, 1051).

agents used are dilute nitric acid, chromic acid mixture or ozone. It is also obtained by the methylation of *p*-hydroxybenzaldehyde. The semi-carbazone melts at 203°–204°, the two modifications of the oxime at 63° and 132° respectively.

Vanillin (*v.* VANILLIN).

Heliotropin (Piperonal) methylene proto-

catechuic aldehyde. White crystals, m.p. 36°; b.p. 236°. Heliotropin has the characteristic odour of heliotrope flowers, but it has only been detected with certainty in the flowers of *Spiræa ulmaria* (Linn.). It was originally synthesised by Fittig and Mielk from piperonylic acid, and was prepared from piperine. Ground pepper is mixed with slaked lime and water, evaporated to dryness and extracted with ether. The residue is boiled with alcoholic potash and the potassium piperate formed oxidised with permanganate. From the filtered solution, heliotropin crystallises out. It is now manufactured by the oxidation of *iso*safrol with permanganate or chromic acid. The product is steam distilled, extracted with ether and purified by means of its bisulphite compound. The yield produced by oxidation of safrole is much less, so that the safrole is converted first to *iso*safrole by boiling with alcoholic potash.

CH : CH·CH₃   CH₂·CH : CH₂

 →

The use of ozone as oxidising agent gives a good yield of a pure product (Otto). It may also be prepared by the action of methylene iodide on protocatechuic aldehyde in presence of alkali.

Since its introduction in 1879, the price has fallen from £150 to 30*s.* per kilo. It must be kept in a cool, dark place since it becomes gradually discoloured on exposure to light; in the hot weather it is conveniently kept in alcoholic solution. It may be identified by a semicarbazone (m.p. 224°–225°), by reduction to piperonyl alcohol (m.p. 51°), or by oxidation to piperonylic acid (m.p. 228°).

KETONES.

The most important members of this class are irone, the odoriferous principle of orris-root ionone, the basis of the synthetic violet perfumes, and jasmone, the ketone isolated by Hesse from jasmine oil, the constitution of which is as yet unknown.
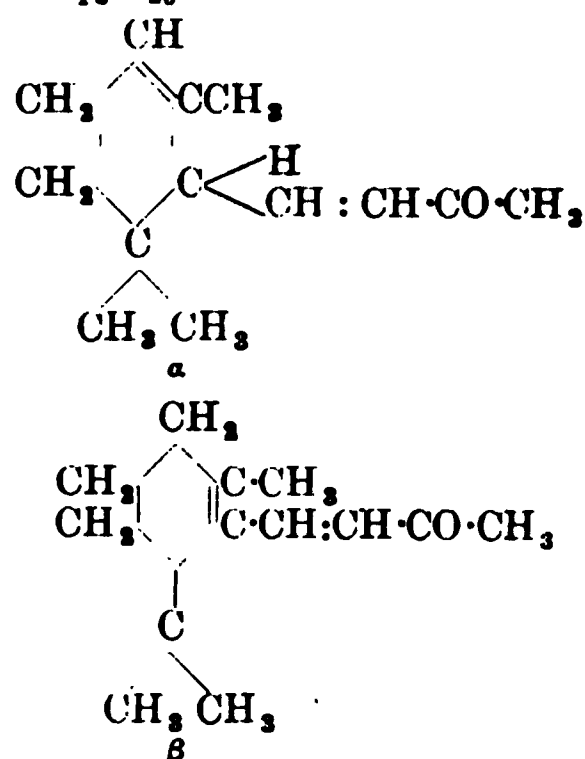
Irone $C_{13}H_{20}O$

b.p. 144° (16 mm.); sp.gr. 0·939 at 20°, $[a]_D$ +40°, n_D 1·50113 (Tiemann and Kruger).

The orris root is extracted with ether and the extracted matter distilled in steam. The volatile fraction contains irone, myristic, and oleic acids and their esters and oleic aldehyde. The acids and esters are removed by treating with alcoholic potash, the aldehydes oxidised by means of silver oxide, and finally the irone separated by conversion into its phenyl hydrazone (Tiemann and Kruger, Ber. 1893, 26, 2675). It may be obtained more conveniently from orris-root oil by fractional distillation. The smell of the pure substance is sharp when concentrated, but if largely diluted, resembles that of violets. Its synthesis has been accomplished by Merling and Welde (Annalen, 1909, 366, 119) who, starting from *iso*propylidene acetoacetic ester, succeeded in obtaining Δ-4-*cyclo*citral; on condensing this with acetone, irone was produced.
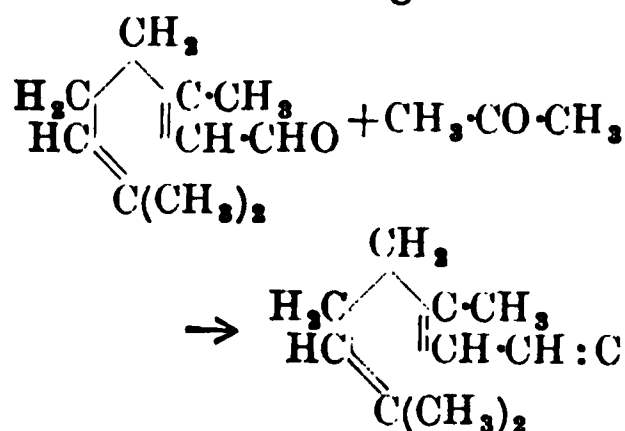
It is characterised by a *p*-bromophenyl hydrazone (m.p. 174°–175°), and an oxime (m.p. 121·5°), crystallising with difficulty.

Ionone $C_{13}H_{20}O$

a-Ionone, b.p. 123°–124° (11 mm.), sp.gr. 0·932 at 20°, n_D 1·4980; *β*-Ionone, b.p. 127°–128·5° (10 mm.), sp.gr. 0·946 at 17°, $n_D^{17°}$ 1·521.

Ionone, obtained by Tiemann and Krüger (Ber. 1893, 26, 2691) in an unsuccessful endeavour to synthesise irone, forms the basis of synthetic violet perfumes. Citral and acetone interact, in the presence of alkaline condensing agents, forming *pseudo*-ionone, a pale yellow strongly refractive oil, boiling at 143°–145° (12 mm.)

→

This, when treated with acids, is converted into a mixture of the isomeric cyclic ketones *a*- and *β*- ionone. As the alkaline condensing agent dilute baryta water may be used, or the dry mixture of citral and acetone may be shaken with dry sodium peroxide (Kayse, D. R. P. 127661), or with PbO, LaO, or borates (Haarman and Reimer, D. R. P. 130457). The proportion of *a*- or *β*- compound produced

be commenced, the test flame being applied once for every rise of one degree in the following manner :—

The slide is slowly drawn open while the pendulum performs three oscillations and is closed during the fourth oscillation.

NOTE.—If it is desired to employ the test apparatus to determine the flashing-point of oils of very low volatility, the mode of proceeding is to be modified as follows :—

The air-chamber which surrounds the cup is filled with cold water to a depth of $1\frac{1}{2}$ inches, and the heating-vessel or water-bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus, and kept there during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120°F. instead of with cold water.[1]

In order to deal with the difficulty arising from the sluggish flow of the convection currents, and the consequent low reading of the thermometer, when viscous samples are tested, and, in addition, to make provision for the testing of

FIG. 10.

solid petroleum mixtures, an Order in Council (Statutory Rules and Orders, 1907, No. 483) was issued on May 7, 1907, the Schedule of which is as follows :—

SCHEDULE.—DIRECTIONS FOR TESTING PETROLEUM MIXTURES.

1. *Liquid Mixtures.* Where the petroleum mixture is wholly liquid, flows quite freely, and does not contain any sediment or thickening ingredient, such mixture shall be tested in the manner set forth in Schedule One to the Petroleum Act, 1879.

2. *Viscous and Sedimentary Mixtures.* Where the petroleum mixture contains an undissolved sediment, as in the case of some metal polishes, which can be separated by filtration or by settlement and decantation, the sediment may be so separated and the decanted liquid may be tested in the manner

[1] A preferable method is to keep the temperature of the water-bath at 130°F. and place water to a depth of a quarter of an inch in the air-space.

purpose, which occupies less space than a lever press.

c. *Percentage of water and dirt.* The percentage of water in paraffin scale may be determined by heating a weighed quantity in an evaporating dish to a temperature somewhat above the boiling-point of water, the melted paraffin being continuously stirred until the

Fig. 33.

whole of the water has been driven off, when the loss in weight is noted. If the quantity of water present is large the percentage may be determined

charge of 50 grams of paraffin) the lower part of which is graduated. In the use of this instrument the greater portion of the melted paraffin may be readily poured off by removing the tube from the heating-bath when the water has separated, and plunging the lower end into cold water so as to seal the water by causing the solidification of a layer of paraffin above it.

Fig. 34.

by distillation or by subsidence, the paraffin being retained in a melted state until the water

Fig. 36.

The operation may then be completed by dissolving the remaining paraffin in warm petroleum spirit (hydrated). In this method of testing, the dirt is usually estimated with the water, but if the proportion of dirt is considerable it should be collected on a filter paper, washed with mineral spirit, dried and weighed.

The following methods of testing Scotch paraffin scale and heavy mineral oils were agreed upon by the chief chemists of the Scottish Mineral Oil Association, Price's Patent Candle Company, and the writer.

Fig. 35.

has separated. Sutherland[1] has introduced a convenient form of apparatus for making the latter test, consisting of a bulbed tube (taking a

[1] J. Soc. Chem. Ind., 1887, 6, 123.

III. Viscosity of Mineral Oil.

9. *Determination of the viscosity of mineral oil.* The instrument known as the 'Redwood' viscometer is that which is to be employed in the determination of the viscosity of mineral oils. The instrument is to be standardised according to the directions given by Mr. Boverton Redwood (J. Soc. Chem. Ind. 5, 127). Ordinary results are to be expressed, as the time in seconds which 50 c.c. of the oil take to flow through the orifice at a temperature of 70°F.

IV. Setting-point of Mineral Oil.

10. *Determination of the setting-point of mineral oil.* This is determined in the following manner. Into a test-tube having a diameter of about 1¼ ins. the oil to be tested is added 'to the depth of about 2 ins.; the tube is then immersed in a freezing mixture, the oil being slowly stirred with a thermometer until it is cooled down considerably below the temperature at which solid paraffin first appears. The tube is then removed from the freezing mixture, the oil constantly stirred with the thermometer, and the point carefully watched at which the last trace of solid paraffin disappears. This operation is repeated with the same sample of oil until two experiments give concordant results, the temperature so found being the setting-point.

7. Gas and fuel oils.

'Gas oils' (mineral oil distillates used in the manufacture of gas for illuminating purposes or for the enrichment of coal-gas) are tested for specific gravity, flash-point, and freedom from water and dirt. In some cases a distillation test designed to secure uniformity in the oils supplied is also carried out.

Oils intended for use as liquid fuel are examined for the presence of water and of solid particles of foreign matter capable of blocking the burners, as well as for specific gravity, flash-point, fluidity at 32°F., calorific value, and percentage of sulphur.

Calorific value. This is best determined by burning one gram in a bomb calorimeter of the Mahler or similar type. Accuracy to within about half of 1 p.c. may be obtained with careful working.[1]

Sulphur. After the determination of the calorific value, the gaseous products of combustion in the bomb are led through a slightly alkaline scrubber, the liquid in which is added to the rinsings of the bomb and the whole precipitated with barium chloride in the usual manner. **B. R.**

PE-TUN-TSE, PE-TUN-SE, or PETUNTZITE

v. China-stone.

PEUCEDANUM (ANETHUM) GRAVEOLENS

(Benth. et Hook.). The common Dill, cultivated in England and the South of Europe. Has a hot sweetish taste; is used in medicine and for flavouring spirituous cordials.
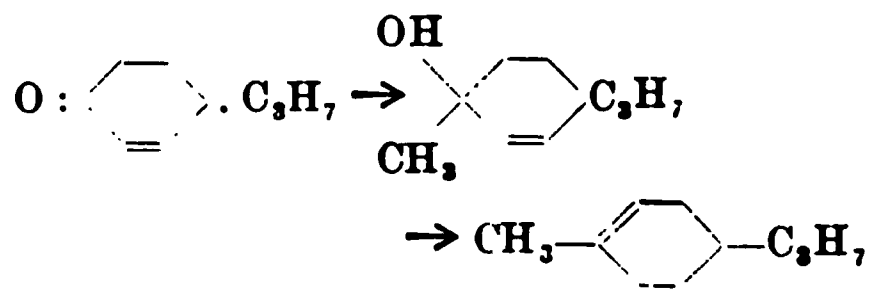
PEWTER *v.* Tin.

PHASEOLUNATIN *v.* Glucosides.

PHELLANDRENE $C_{10}H_{16}$ is a terpene which occurs in many oils such as that of *Eucalyptus amygdalina* (Labill.) (Baker and Smith, J. Soc.

[1] A full translation into English of the descriptive pamphlet issued by the makers of the Mahler bomb is included in Hick's Mineral Oil Testing (Griffin).

Chem. Ind. 1899, 302; Wallach, Annalen, 1905, 343, 28): in cinnamon oil (Dayk, Chem. Zentr. 1896, ii. 358; Schimmel & Co., *ibid.* 1910, i. 1720); in the oils of schinus molle (Wallach, *ibid.* 1905, ii. 674); of *Juniperus phoenicea* (Linn.) (Rodié, Bull. Soc. chim. 1906, [iii.]35, 922); of *Abies sibirica* (Ledeb.) (Schindelmeiser, Chem. Zeit. 1907, 31, 759); of the sassafras bark and leaves (Power and Klebber, Chem. Zentr. 1897, ii. 42); in the seeds of *Monodora Grandiflora* (Benth.) (Leimbach, *ibid.* 1909, ii. 1870); in elemi oil (Glover, *ibid.* 1907, i. 1794); in the resins of elemi wood (*Canarium luzonicum* [Miq.])[r](Wallach and Rheindorf, Annalen, 1892, 271, 310; Bacon, Chem. Zentr. 1909, ii. 1448); in bitter fennel oil (Cahours, Annalen, 1842, 41, 74; Wallach, *ibid.* 1887, 239, 40; *ibid.* 1904, 336, 10); in water fennel oil (*Oenanthe Phellandrium* (Lam.)) from which the name is derived (Pesci, Gazz. chim. ital. 1886, 16, 225), and in many other oils (*see* Biochemisches Handlexikon, 1910, vii. 295).

It is one of the most unstable of the terpenes, and occurs in two modifications, the α- and β- or *pseudo*, the former of which is usually present in greater quantity than the latter. Neither of these has, however, ever been obtained quite pure (Kondakoff, J. pr. Chem. 1908, [ii.] 78, 42).

α-Phellandrene exists in dextro- and lævorotatory modifications. The chief sources of *d*-α-phellandrene are bitter fennel, elemi, and schinus oil. It is also the chief constituent in the dry distillation of certain elemi resins, whilst the chief source of *l*-α-phellandrene is eucalyptus oil (Wallach, Annalen, 1904, 336, 10). The purest natural α-phellandrene so far obtained has b.p. 61°/11 mm., sp.gr. 0·844 at 19° (*d*−α), and b.p. 65°/12 mm., sp.gr. 0·846, at 19° (*l*−α), at ordinary pressure the b.p. is 173°–176°. The optical rotation depends on the source of the phellandrene. α-Phellandrene has been synthesised from *iso*propyl-Δ²-hexenone by treating the latter with magnesium methyl iodide thus:

$$O : \underset{CH_3}{\overset{OH}{\langle \ \rangle}} . C_3H_7 \rightarrow \underset{CH_3}{\overset{OH}{\diagdown}} \langle \ \rangle C_3H_7$$

$$\rightarrow CH_3 - \langle \ \rangle - C_3H_7$$

(Wallach, Annalen, 1908, 359, 265; *ibid.* 362, 281). It has b.p. 175°–176° (decomp.), sp.gr. 0·841 at 22°.

α-Phellandrene has also been synthesised from Δ⁶-menthene-2-one by treating it with phosphorus pentachloride and reducing the product thus obtained with zinc-dust in methyl alcohol solution, or by reducing menthenone-2-oxime with zinc-dust and glacial acetic acid, and distilling the Δ⁶-mentheneamine so formed *in vacuo* with phosphoric acid. The α-phellandrene so obtained has b.p. 66°/14 mm., 70°/15 mm., sp.gr. 0·8473 at 21° $a_D + 45°$ (Harries and Johnson, Ber. 1905, 38, 1832; *see* also Kondakoff and Schindelmeiser, J. pr. Chem. 1905, [ii.] 72, 193; 1907, [ii.] 75, 141).

α-Phellandrene combines directly with two atoms of bromine forming a dibromide which, when boiled with alcoholic potash, yields cymene (Wallach and Herbig, Annalen, 1895, 287, 371; Bacon, *l.c.*). When treated with alcoholic

after removal of acid and basic constituents, the residue is freed from fluorene and diphenylene oxide by fusion with caustic potash at 300°, followed by extraction with hot water. The residue is then distilled to obtain the pure hydrocarbon (Akt. Teer- u. Erd-Oel Ind. D. R.-P. 130679 ; Eng. Pat. 5047 of 1901 ; cf. Kraemer and Weissgerber, Ber. 1901, 34, 1665).

On the laboratory scale, phenanthrene is purified conveniently by conversion in alcoholic solution into the *picrate*, which crystallises in golden-yellow needles, m.p. 143°-145°, and on treatment with ammonia yields the pure hydrocarbon (Limpricht, Ber. 1873, 6, 532).

Properties.—Phenanthrene crystallises in colourless scales, m.p. 100°, b.p. 340°. It is insoluble in water, but readily soluble in hot alcohol, ether, carbon disulphide, acetic acid, or benzene, showing blue fluorescence in solution. 100 parts of toluene dissolve 33·02 parts at 16·5° ; 100 parts of absolute alcohol dissolve 2·62 parts at 16° ; or 10·08 parts at 78° (Bechi, Ber. 1879, 12, 1978) ; and 100 parts of 95 p.c. alcohol dissolve about 2 parts at 13°-14° (Graebe, Annalen, 1873, 167, 136).

Reactions.—(1) Oxidising agents convert phenanthrene into *phenanthraquinone*, or by further oxidation into *diphenic acid* (Fittig and Ostermayer, l.c.), but with a large excess of 100 p.c. sulphuric acid and some mercury at 300° *phthalic acid* is obtained (Bad. Anilin- u. Soda-Fab. D. R.-P. 91202 ; Eng. Pat. 18221 of 1906).

(2) Chlorination in presence of halogen carriers leads to the production of 9 : 10-*dichlorophenanthrene*, needles, m.p. 160°-161° (J. Schmidt and Ladner, Ber. 1904, 37, 4403), and of 2 : 9 : 10-*trichlorophenanthrene*, needles, m.p. 123°-124° (Schmidt and Schall, *ibid.* 1906, 39, 3892).

(3) With bromine in the cold it forms the *dibromide*, prisms, m.p. 98°, which, heated at its melting point, or with water, decomposes into 9 (10)-*bromophenanthrene*, prisms, m.p. 63° (Fittig and Ostermayer, Annalen, 1873, 166, 363 ; Hayduck, l.c. ; Zetter,[1] Ber. 1878, 11, 165 ; Austin, Chem. Soc. Trans. 1908, 93, 1763). Bromination in boiling chloroform solution leads to the formation of 3 : 9- (or 10)-dibromophenanthrene, needles, m.p. 146° (Schmidt and Ladner, Ber. 1904, 37, 3577) from phenanthrene, but of 2 : 7-*dibromophenanthrene*, needles, m.p. 199°-200°, from a-tetrahydrophenanthrene (Schmidt and Mezger, *ibid.* 1907, 40, 4562).
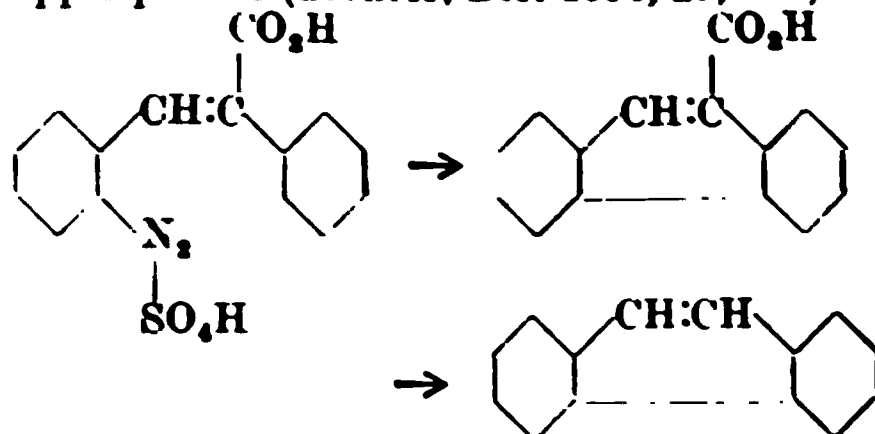
(4) By nitric acid, it is converted into nitro derivatives like naphthalene and not oxidised to quinone like anthracene.

Constitution and syntheses.—The structural formula assigned to phenanthrene at the head of this article was adopted originally to exhibit the relationship existing between the hydrocarbon and diphenic acid, its oxidation product (Fittig and Ostermayer, l.c. ; Schultz, Annalen, 1879, 196, 1 ; 1880, 203, 95), or phthalic acid (cf. Anschütz and Japp, Ber. 1878, 11, 211). It has been confirmed by several syntheses, from among which three may be selected for reference as establishing the presence of specific radicles or linkings :—
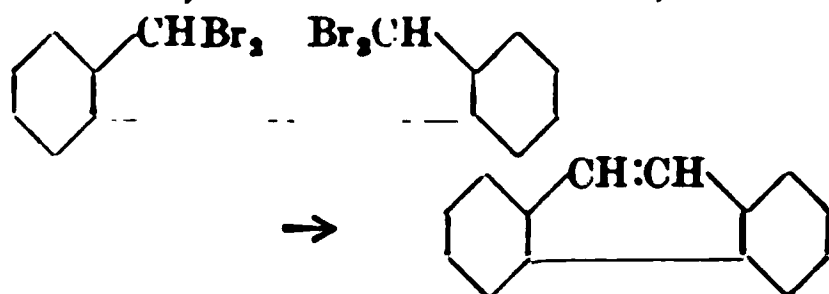
(i.) Relationship to ethylene : Production

of phenanthrene by distilling phenanthrene-9-carboxylic acid obtained by the interaction of diazotised a-phenyl-o-aminocinnamic acid and copper powder (Pschorr, Ber. 1896, 29, 496).

$$CO_2H \qquad CO_2H$$

(ii.) Relationship to diphenyl : Production of phenanthrene by debrominating ωωω'ω'-tetrabromo-2 : 2'-ditolyl by means of sodium (Kenner and Turner, Chem. Soc. Trans. 1911, 99, 2112).

(iii.) Relationship to naphthalene : Production of 4-hydroxyphenanthrene by heating β-naphthylisocrotonic acid, prepared from β-naphthaldehyde by the Perkin reaction (Ludewig, Annalen, 1911, 379, 361).[1]

$$+H_2O$$

Pschorr's method has proved to be of wide application in the synthesis of phenanthrene derivatives of known constitution from substituted a-phenyl-o-aminocinnamic acids, and, coupled with the investigations of Vongerichten and of Knorr, has made it possible for the relationship between phenanthrene and the morphine group of opium alkaloids to be elucidated.

Chemical activity in the phenanthrene molecule is manifested chiefly at the ethylenic double linking, shown between carbon atoms numbered 9 and 10 in the formula at the head of this article. Here the addition of hydrogen and bromine takes place, here oxidation leading to the production of phenanthraquinone occurs, and here disruption of the molecule follows when more powerful oxidising agents are used—as in the formation of diphenic acid. For the purpose of determining orientation in the phenanthrene molecule, oxidation to diphenic acid is important, as—when substituents occur in positions other than 9 or 10 or 9 and 10—they are found in corresponding positions in the resulting diphenic acids.

Phenanthrene has little value in technical chemistry, but its relationship to some of the alkaloids of opium and of *Corydalis* is of much interest. These alkaloids are methoxy or hydroxy derivatives of tetra- or

[1] Zetter, also, has described two dibromophenanthrenes, but one of them—the β-compound—is now known to be β-dibromofluorene (Werner and Egger, Ber. 1904, 37, 3027).
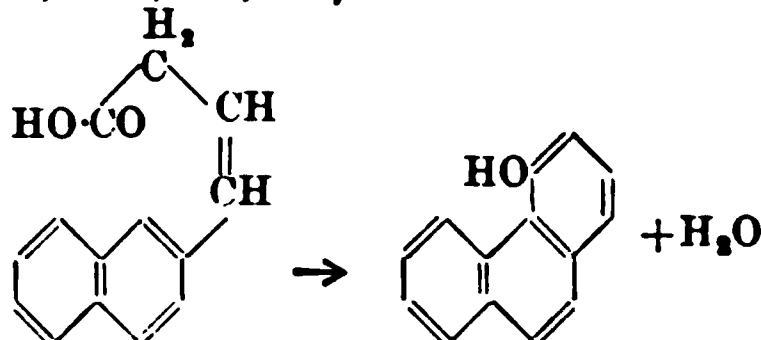
[1] Although phenanthrene can be synthesised from naphthalene, the reverse operation has not been accomplished, the lateral rings remaining intact until the middle ring has been broken down by oxidising agents.

NITROPHENANTHRENES.

Of the five nitrophenanthrenes the 1-iso-meride has not yet been prepared (J. Schmidt and Heinle, Ber. 1911, 44, 1490).

Earlier work on the nitration of phenanthrene with a large excess of fuming nitric acid led to the isolation of three compounds, termed α- (m.p. 73°-75°), β- (m.p. 126°-127°), and γ- (m.p. 170°-171°) nitrophenanthrenes (G. A. Schmidt, Ber. 1879, 12, 1153). It has been shown that of these compounds the α- and γ- are identical respectively with 4- and 3-nitro-phenanthrenes, but that the β-compound is a nitro derivative not of phenanthrene, but of fluorene, which accompanies this hydrocarbon in coal-tar (J. Schmidt and Heinle, l.c.).

For the production of nitrophenanthrenes J. Schmidt has employed two methods. In one, nitration is effected by nitric acid (sp.gr. 1·45) in presence of a mixture of acetic acid and acetic anhydride, leading to the formation of the four isomerides. A summary of the properties and yields of these substances, as recorded by J. Schmidt and Heinle, is given in the table—

NO$_2$	Yield (approx.)	Crystallisation from alcohol	M.p.	Picrate
2-	20 p.c.	pale yellow rosettes	99°	none
3-[1]	2 p.c.	deep yellow needles	170°-171°	none
4-	20 p.c.	reddish yellow needles	80°-82°	none
9-	60 p.c.	orange yellow needles	116°-117°	98°-99°

In the second method use is made of one of the two additive compounds which phenanthrene, dissolved in benzene, forms with the nitrous gas obtained by the interaction of nitric acid and arsenious oxide. This substance, nitrodihydro-phenanthrene oxide (m.p. 154°-155°), is converted by sodium methoxide into 9-nitro-phenanthrene (J. Schmidt, Ber. 1910, 33, 3257):

$$\begin{array}{c} C_6H_4{\cdot}CH \underline{\quad\quad} O \underline{\quad\quad} CH{\cdot}C_6H_4 \\ | \quad\quad\quad\quad\quad\quad\quad | \\ C_6H_4{\cdot}CH(NO_2)\,(NO_2)CH{\cdot}C_6H_4 \end{array} \rightarrow 2\begin{array}{c} C_6H_4{\cdot}CH \\ \| \\ C_6H_4{\cdot}C{\cdot}NO_2 \end{array} + H_2O$$

Corresponding with this 9-nitro derivative, 9-nitro-9 : 10-dihydrophenanthrene, a yellow crystalline compound, decomposing at 100°, is obtained on mixing phenanthrene in dry powder with the liquefied nitrous gas (J. Schmidt, D. R.-P. 129990 of 1901).

AMINOPHENANTHRENES.

Four aminophenanthrenes (phenanthryl-amines) are known corresponding in orientation with the nitrophenanthrenes. Three methods have been used for their preparation :—

(i.) Reduction of the nitro compound by alcoholic ammonium sulphide (G. A. Schmidt, Ber. 1879, 12, 1156), or stannous chloride and hydrochloric acid (J. Schmidt and Strobel, ibid. 1901, 34, 1464), or zinc dust and alcoholic ammonia (J. Schmidt and Heinle, ibid. 1911, 44, 1498).

(ii.) Heating the hydroxy compound at temperatures above 200° with ammonia (Japp and Findlay, Chem. Soc. Trans. 1897, 71, 1123;

Pschorr and Schröter, Ber. 1902, 35, 2728), or ammonio-calcium chloride, or—for the acetyl compound—ammonium chloride, sodium acetate, and acetic acid (Werner and Kunz, Ber. 1901, 34, 2525).

(iii.) Conversion of the carboxylic acid successively into the hydrazide, azide, and urethane, which is then heated with ammonia (Pschorr and Schröter, l.c.; Pschorr, Einbeck, and Spangenberg, Ber. 1907, 40, 2000).

The crystalline character and m.p. of each base and the m.p. of its acetyl and benzoyl derivatives are given in the table—

—	Base	Acetyl	Benzoyl
2-	crystals, 85°	225°-226°	—
3-α-	leaflets, 143°	} 200°-201°β	213°-214°β
β-	leaflets, 87·5°		
4-	needles, 105°	190°	224°
9-α-	needles, 138°	} 207°-208°α	190°α
β-	crystals, 104°		

As shown in the table, 3-aminophenanthrene (Werner and Kunz, l.c.; Werner, Annalen, 1902, 321, 312; cf. J. Schmidt and Sauer, Ber. 1911, 44, 3247) and 9-aminophenanthrene (J. Schmidt and Heinle, l.c.) exist in two forms—one stable, the other labile and convertible into it by being heated or kept for some time or acetylated. Both forms of each compound give the same acetyl or benzoyl derivative, from which by hydrolysis the stable form of the base (indicated by the Greek letter) is obtained. The nature of the isomerism has not been established, but it has been attributed to rearrangement of the linkings in the phenanthrene molecule in view of the fact that the two forms of the 9-isomeride have the same molecular weight (J. Schmidt and Heinle, l.c.).

Diazotisation of β-3-aminophenanthrene (J. Schmidt, Ber. 1901, 34, 3534; cf. Werner and Kunz, l.c.), and of 9-aminophenanthrene [1] (J. Schmidt and Strobel, Ber. 1903, 36, 2517) has been effected—in the latter case with the accompanying production of azoxy and azo compounds. But difficulty has been experienced in diazotising 2-aminophenanthrene (Werner and Kunz, l.c.), although 2-amino- (like 8-amino-) phenanthrene-9-carboxylic acid forms a diazo compound apparently with ease (Pschorr, Ber. 1906, 39, 3121).

The oxime and dioxime of phenanthra-quinone, on reduction with stannous chloride, yield 9 : 10-aminohydroxyphenanthrene (Vahlen's 'morphigenine,' cf. D. P. Anm. V. 3840 of 1902; Ber. 1902, 35, 3044) and 9 : 10-diamino-phenanthrene respectively (Pschorr and Schröter, ibid. 3733). The former, when heated with water or dilute acid, is converted into 9-amino-phenanthrene (Schmidt, D. R.-P. 141422 of 1902).

HYDROXYPHENANTHRENES.

The hydroxy derivatives of phenanthrene (phenanthrols) have been investigated largely as a consequence of the relationship which has been established between them, and certain of the opium and Corydalis alkaloids. In many cases the constitution of the hydroxy-

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[1] 3-Nitrophenanthrene is obtained in better yield by nitrating phenanthrene with nitric acid of sp.gr. 1·56 at 0° (J. Schmidt and Heinle, l.c.).
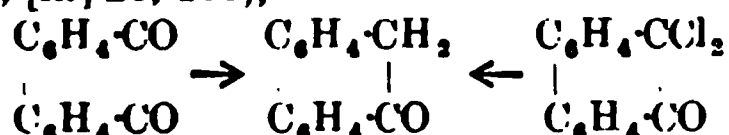
[1] The presence of two forms of the 9-isomeride in the reduction product of 9-nitrophenanthrene was not recognised until later (J. Schmidt and Heinle, l.c.), and there is no information to show whether both forms, or only the α-derivative can be diazotised.

phenanthrenes has been determined by Pschorr's synthetical method, which has shown itself to be of the first importance in the study of the degradation products of these alkaloids. In others, the constitution assigned depends on that of the sulphonic acids, from which some of the hydroxy derivatives have been obtained by fusion with caustic alkali (cf. Werner, Annalen, 1902, 321, 276). The constitution, crystalline character, and melting-point of the hydroxyphenanthrenes and of their ethers are given in the table :—

OH in	Hydroxyphenanthrenes and their ethers.	References.
1	Has not been isolated. *Methyl ether*, needles, m.p. 105°–106°; gives *picrate*, needles, m.p. 153°.	Pschorr, Wolfes and Buckow (Ber. 1900, 33, 162).
2	Forms scales, m.p. 169°; couples with diazotised bases; gives *acetate*, needles, m.p. 142°–143°, and *benzoate*, leaflets, m.p. 139°–140°. *Methyl ether*, leaflets, m.p. 100°–101°; gives *picrate*, needles, m.p. 124°. *Ethyl ether*, leaflets, m.p. 112°.	Werner and Kunz (Ber. 1901, 34, 2524); Pschorr and Klein (*ibid.*, 4005); Werner and Rekner (Annalen 1902, 321, 305); Henstock (Chem. Soc. Trans. 1906, 89, 1528).
3	Forms needles, m.p. 122°–123°; couples with diazotised bases; gives *picrate*, m.p. 159°, *acetate*, plates, m.p. 115°–116°, and *benzoate*, needles, m.p. 119°. *Methyl ether*, plates, m.p. 63°; gives *picrate*, red needles, m.p. 124·5°. *Ethyl ether*, m.p. 46°.	Pschorr, Wolfes and Buckow (*l.c.*); Pschorr and Sumuleanu (Ber. 1900, 33, 1821); Werner and Kunz (*l.c.*); Schmidt (Ber. 1901, 34, 3535); Pschorr (*ibid.* 4006).
4	Crystalline, m.p. 106°–109°; gives *acetate*, leaflets, m.p. 58°–59°. *Methyl ether*, leaflets, m.p. 68°; gives *picrate*, red needles, m.p. 187°–188°.	Pschorr and Jaeckel (Ber. 1900, 33, 1826); Ludewig (Annalen, 1911, 379, 361).
9 (10)	Forms large needles, m.p. 152°–153°; couples with diazotised bases; gives *picrate*, red needles, m.p. 183°, *acetate*, needles, m.p. 77°, and *benzoate*, needles, m.p. 96°–97°. *Methyl ether*, needles, m.p. 96°–97°.	Japp and Findlay (Chem. Soc. Trans., 1897, 71, 1115); Werner and Frey (Annalen, 1902, 321, 298); Pschorr and Schröter (Ber. 1902, 35, 2728).
2 : 3	Has not been isolated. *Dimethyl ether*, leaflets, m.p. 131°; gives *picrate*, needles, 127°–128°.	Pschorr and Buckow (Ber. 1900, 33, 1829).
3 : 4	M o r p h o l, forms long needles, m.p. 143°; gives *diacetate*, needles, m.p. 159°. 3-*Methyl ether*, needles, m.p. 65°; gives *picrate*, red needles, m.p. 150°, and *acetate*, needles, m.p. 131°. 4-*Methyl ether*, oil; gives *acetate*, needles, m.p. 93°–94°. *Dimethyl ether*, leaflets, m.p. 44°; gives red *picrate*, m.p. 105°–106°, and *dibromide*, m.p. 123°.	Fischer and Vongerichten (Ber. 1886, 19, 793); Knorr (*ibid.* 1892, 25, 1147; 1894, 27, 1148); Pschorr and Sumuleanu (*ibid.* 1900, 33, 1819, 1823); Vongerichten (*ibid.* 352, 1825); Knorr (*ibid.* 1904, 37, 3497); Knorr and Pschorr (*ibid.* 1905, 38, 3178); Pschorr and Dickhäuser (Annalen, 1910, 373, 81).
9 : 10	Forms needles, m.p. 146°; gives *monoacetate*, needles, m.p. 168°–170°; *diacetate*, flat prisms, m.p. 202°, and *dibenzoate* m.p. 230°–231°.	Graebe (Annalen, 1873, 167, 146); Japp and Klingemann (Chem. Soc. Trans. 1893, 63, 771); Pschorr (Ber. 1902, 35, 2736, 3124), Knesch (D. R.-P. 151981 of 1903.
3 : 4 : 5	Forms scales, m.p. 148°. *Trimethyl ether*, m.p. 90°; gives *picrate*, brown scales or needles, m.p. 167°.	Vongerichten (Ber. 1906, 39, 1720); Pschorr and Koch (Annalen, 1912, 391, 54).
3 : 4 : 6	Has not been isolated. 3-*Methyl ether*, oil; gives *diacetate*, m.p. 162°–163°. 3 : 6-*Dimethyl ether* (t h e b a o l), m.p. 94°; gives *acetate*, m.p. 118°–120°. *Trimethyl ether*, oil; gives *picrate*, m.p. 109°–110°.	Freund (Ber. 1897, 30, 1389); Pschorr, Seydel and Stöhrer (*ibid.* 1902, 35, 4406); Vongerichten (*ibid.* 4411); Knorr (*ibid.* 1904, 37, 3499); Pschorr and Rettberg (Annalen, 1910, 373, 66).
3 : 4 : 8	Has not been isolated. 8-Methyl ether; *diacetate*, m.p. 155°–156°. 8 : 4-*Dimethyl ether*, prisms, m.p. 182°–183°. 4 : 8-*Dimethyl ether* (a-4-t h e b a o l), leaflets, m.p. 164°–165°; gives *acetate*, prisms, m.p. 96°–97°. *Trimethyl ether*, leaflets, m.p. 138°; gives *picrate*, red needles, m.p. 129°, and *dibromide*, needles, m.p. 139°–140°. 3 : 4-*Dimethyl-8-ethyl ether*, leaflets, m.p. 100°; gives *picrate*, red needles, m.p. 119°.	Pschorr (Ber. 1900, 33, 183); Pschorr Einbeck and Spangenberg (Ber. 1907, 40, 2000); Pschorr and Busch (*ibid.* 2001); Knorr and Hoerlein (*ibid.* 2039); Pschorr and Loewen (Annalen, 1910, 373, 73); Pschorr and Zeidler (*ibid.* 75).
3 : 4 : 9 (or 10)	Has not been isolated. 3-Methyl ether; *diacetate*, needles, m.p. 202°–204°.	Knorr and Schneider (Ber. 1906, 39, 1420); Pschorr, Kuhtz and Roth (*ibid.* 3137).
1 : 3 : 5 : 6	3 : 5 : 6-*Trimethyl ether*, no description given. *Tetramethyl ether*, needles, m.p. 108°–109° gives *picrate*, red needles, m.p. 147°–148°.	Pschorr and Rettberg (*l.c.*); Pschorr and Knoeffler (Annalen, 1911, 382, 50.

Among these hydroxyphenanthrenes there are several, about which the information given in the table needs to be supplemented to make clear their properties and relationships.

9- (or 10-) **Hydroxyphenanthrene**, also known as phenanthrone, affords an example of keto-enolic isomerism in the phenanthrene series. It can be obtained from phenanthraquinone by partial reduction with hydriodic acid (Japp and Klingemann, Chem. Soc. Trans. 1893, 63, 770), or from dichlorophenanthrone by reduction with iron and acetic acid (Lachowicz, J. pr. Chem. 1883, [ii.] 28, 168), and is therefore a ketone
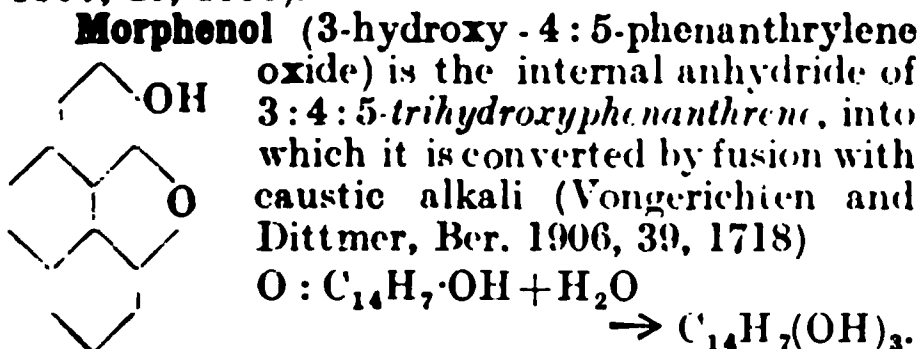
$$C_6H_4 \cdot CO \qquad C_6H_4 \cdot CH_2 \qquad C_6H_4 \cdot CCl_2$$
$$C_6H_4 \cdot CO \qquad C_6H_4 \cdot CO \qquad C_6H_4 \cdot CO$$

But its formation from phenanthrene-9-sulphonic acid by fusion with caustic alkali, its solubility in alkali, and its conversion into an *ortho-azo* compound (*phenanthraquinonehydrazone*, m.p. 165°) by coupling with diazotised aniline (Werner and Frey, Annalen, 1902, 321, 298), show it to be phenolic under other conditions.

Hydroxyphenanthrenes from opium alkaloids.

The degradation of opium alkaloids into nitrogen compounds containing relatively few carbon atoms and into derivatives of hydroxy-phenanthrene free from nitrogen, has been accomplished by Hofmann's method of exhaustive methylation (Ber. 1881, 14, 494, 663), the products being decomposed by hydrogen chloride (Knorr, *ibid.* 1894, 27, 1147), acetic anhydride (Fischer and Vongerichten, *ibid.* 1886, 19, 792), heat (Schrötter and Vongerichten, *ibid.* 1882, 15, 1485), or hot caustic soda solution (Freund, *ibid.* 1897, 30, 1379). A list of decomposition products of this type is given by Knorr and Pschorr, Ber. 1905, 38, 3174. The following summary indicates the sources of the more important nitrogen-free degradation products of opium and *Corydalis* alkaloids.

3 : 4-Dihydroxyphenanthrene or **morphol** is formed when acetylmorphine methiodide and its 3-*methyl ether* when acetylcodeïne methiodide are heated with acetic anhydride (Fischer and Vongerichten, Ber. 1886, 19, 792 ; Knorr, *ibid.* 1889, 22, 181, 1113 ; Vongerichten, *ibid.* 1896, 29, 65 ; 1897, 30, 2439), or morphenol methyl ether is reduced by sodium and alcohol (Vongerichten and Dittmer, *ibid.* 1906, 39, 1719). By the degradation of apomorphine the *dimethyl ether* of *morphol-8-carboxylic acid* has been obtained, convertible into morphol dimethyl ether (Pschorr, Jaeckel and Fecht, Ber. 1902, 35, 4392 ; Pschorr, Einbeck and Spangenberg, *ibid.* 1907, 40, 1998).

Morphenol (3-hydroxy-4 : 5-phenanthrylene oxide) is the internal anhydride of 3 : 4 : 5-*trihydroxyphenanthrene*, into which it is converted by fusion with caustic alkali (Vongerichten and Dittmer, Ber. 1906, 39, 1718)

$$O : C_{14}H_7 \cdot OH + H_2O$$
$$\rightarrow C_{14}H_7(OH)_3.$$

It is obtained from β-methylmorphimethine methiodide (Vongerichten, Ber. 1898, 31, 54 ; 1901, 34, 2722), or from morphine without the isolation of the morphimethine (Vongerichten, *ibid.* 1900, 33, 358) ; or from morphenol methyl ether by demethylation with hydriodic acid (Vongerichten, *ibid.* 1898, 31, 3202). It forms needles, m.p.145°, gives no colouration in alcoholic solution with ferric chloride, dissolves in caustic soda, giving a yellow solution with blue fluores-

cence, and does not couple with diazotised bases. On reduction it yields *morphol* (Vongerichten, Ber. 1899, 32, 1522).

Its *methyl ether* forms needles, m.p. 65° (*cf.* Knorr, Ber. 1889, 22, 184 ; Vongerichten, *ibid.* 1898, 31, 54 ; 1900, 33, 358 ; Schryver and Lees, Chem. Soc. Trans. 1901, 79, 578) ; *acetate*, needles, m.p. 140° ; and *benzoate*, needles, m.p. 123° (Vongerichten, *l.c.*).

3 : 4 : 6-Trihydroxyphenanthrene. The 3-*methyl ether* is obtained from codeïnone (Knorr, Ber. 1903, 36, 3074), and from codeïnone methiodide (Knorr, *ibid.* 1904, 37, 3501). The 3 : 6-*dimethyl ether* or **thebaol** results from boiling thebaïne with acetic anhydride (Freund, Ber. 1897, 30, 1386), and the *trimethyl ether* when the silver salt of the 8-carboxylic acid, obtained from morphothebaïne, is decomposed by heat (Pschorr and Rettberg, Annalen, 1910, 373, 65).

3 : 4 : 8-Trihydroxyphenanthrene. The 8-*methyl ether* is formed from ψ-*iso*-codeïne methiodide (Knorr and Hoerlein, Ber. 1907, 40, 2039, 3350) ; and the *trimethyl ether* from the 5-carboxylic acid obtained from thebenine (Pschorr and Loewen, Annalen, 1910, 373, 71).

3 : 4 : 9- (or 10-)Trihydroxyphenanthrene. The *diacetate* of the 3-*methyl ether* is formed when hydroxymethylmorphimethine (Knorr and Schneider, Ber. 1906, 39, 1420) or dichloromethylmorphimethine (Pschorr, *ibid.* 3137) is heated with acetic anhydride.

Vinylhydroxyphenanthrenes.

As primary products of the Hofmann degradation of certain opium and *Corydalis* alkaloids, the following vinylmethoxyphenanthrenes have been obtained, which on oxidation yield the corresponding methoxyphenanthrenecarboxylic acids.

5-*Vinyl*-3 : 4 : 8-*trimethoxyphenanthrene*, from thebenine, forms tablets, m.p. 122·5° ; *picrate*, red tablets, m.p. 110° (Pschorr and Massaciu, Ber. 1904, 37, 2789). The 8-*ethoxy* derivative forms plates, m.p. 78° (Pschorr and Loewen, Annalen, 1910, 373, 72).

8-*Vinyl*-3 : 4-*dimethoxyphenanthrene*, from *apo*morphine, forms rhombic prisms, m.p. 80° ; *picrate*, violet needles, m.p. 128° (Pschorr, Jaeckel and Fecht, Ber. 1902, 35, 4391 ; *cf.* Pschorr, *ibid.* 1906, 39, 3124).

8-*Vinyl*-3 : 4 : 6-*trimethoxyphenanthrene*, from morphothebaïne, forms prisms, m.p. 60°-61° ; *picrate*, reddish-violet needles, m.p. 125°-126° (Knorr and Pschorr, Ber. 1905, 38, 3157 ; Pschorr and Rettberg, Annalen, 1910, 373, 65).

8-*Vinyl*-3 : 4-*dimethoxy*-5 : 6-*methylenedioxy-phenanthrene*, from bulbocapnine, forms yellow needles, m.p. 101° (Gadamer and Kuntze, Arch. Pharm. 1911, 249, 630).

PHENANTHRENECARBOXYLIC ACIDS.

Phenanthrenecarboxylic acids have been prepared by hydrolysis of the nitriles obtained from the three phenanthrenesulphonic acids on distillation with potassium cyanide or ferrocyanide (Schultz and Japp, Ber. 1877, 10, 1661 ; Japp, Chem. Soc. Trans. 1880, 37, 83 ; Werner and Kunz, Annalen, 1902, 322, 323). Synthetically Pschorr has obtained the 9-carboxylic acid (Ber. 1896, 29, 496), and the 8 : 9-dicarboxylic acid, the latter of which readily forms a well-crystallised anhydride (m.p. 283°-284°), and exhibits

the behaviour of a naphthalene *peri-* derivative (*ibid.* 1906, 39, 3107).

Phenanthrene - 2 - carboxylic acid, needles, m.p. 254°; *nitrile*, granules, m.p. 105°; forms *phenanthraquinone-2-carboxylic acid* on oxidation.

Phenanthrene-3-carboxylic acid ([α-] acid), scales, m.p. 269°, forms the *barium salt*, $BaA_2,7H_2O$, sparingly soluble needles; *sodium salt*, $NaA,4H_2O$, easily soluble scales; *amide*, scales, m.p. 227°-228°; *nitrile*, needles, m.p. 102°; and yields *phenanthraquinone-3-carboxylic acid* on oxidation.

Phenanthrene-9-(10-)carboxylic acid ([β-] acid), needles, m.p. 250°-252°, gives the *barium* salt $BaA_2,6H_2O$, sparingly soluble tablets; *sodium* salt, $NaA,5H_2O$, easily soluble rhombic tablets; *amide*, needles, m.p. 226°; *nitrile*, needles, m.p. 103°; and yields *phenanthraquinone* on oxidation.

HYDROXYPHENANTHRENECARBOXYLIC ACIDS.

Hydroxyphenanthrenecarboxylic acids have been obtained (*a*) from hydroxyphenanthrenes by the Kolbe method with carbon dioxide; (*b*) from alkaloids by oxidation of vinylhydroxyphenanthrenes; (*c*) synthetically by Pschorr's method from substituted cinnamic acids. As will be seen from the following summary, in few cases only have salts been analysed, or esters described.

(i) **Hydroxyphenanthrenecarboxylic acids**, [OH : CO_2H].
2 : 3 (?). Yellow needles, m.p. 277° (decomp.); *acetate*, needles, m.p. 210° (Werner and Kunz, Ber. 1902, 35, 4425); *methyl* ester, needles, m.p. 126°.
2 : 9 Prisms, m.p. 278°: *acetate*, plates, m.p. 223° (Pschorr and Quade, Ber. 1906, 39, 3123).
3 : 2 (?) Yellow prisms, m.p. 303° (decomp.); *acetate*, needles, m.p. 207°-208°: *methyl* ester, needles, m.p. 171° (Werner and Kunz, *l.c.*).

(ii) **Methoxyphenanthrenecarboxylic acids**, [OMe : CO_2H].
2 : 9 Colourless needles, m.p. 228° (Pschorr, Ber. 1901, 34, 4002).
4 : 9 Needles, m.p. 224° (Pschorr and Jaeckel, Ber. 1900, 33, 1827).
1 : 10 Yellow leaflets, m.p. 215° (Pschorr, Wolfes and Buckow, Ber. 1900, 33, 169).
3 : 10 Needles, m.p. 239° (*ibid.* 174).

(iii) **Hydroxymethoxyphenanthrenecarboxylic acids**, [OH : OMe : CO_2H].
3 : 4 : 9 Needles, m.p. 214°-216° (Pschorr and Sumuleanu, Ber. 1900, 33, 1822).
4 : 3 : 9 Needles, m.p. 264°: *acetate*, m.p. 244° (Pschorr and Vogtherr, Ber. 1902, 35, 4414).

(iv) **Dimethoxyphenanthrenecarboxylic acids**, [OMe : OMe : CO_2H].
2 : 3 : 9 Needles, m.p. 270° (Pschorr and Buckow, Ber. 1900, 33, 1830).
3 : 4 : 8 Yellow needles, m.p. 196°: *ethyl* ester, prisms, m.p. 81°-83°; *hydrazide*, needles, m.p. 194°-195° (Pschorr, Jaeckel and Fecht, Ber. 1902, 35, 4392; Pschorr, Einbeck and Spangenberg, *ibid.* 1907, 40, 1999).
3 : 4 : 9 Needles, m.p. 227°-228° (Pschorr and Sumuleanu, Ber. 1900, 33, 1819).

(v) **Hydroxydimethoxyphenanthrenecarboxylic acids**, [OH : OMe : OMe : CO_2H].
3 : 4 : 8 : 9 Six-sided plates, m.p. 231°: *acetate*, prisms, m.p. 220°-227° (Pschorr, Ber. 1900, 33, 180).
4 : 3 : 6 : 9 Leaflets, m.p. 254°-256°: *acetate*, m.p. 201°-203° (Pschorr, Seydel and Stöhrer, Ber. 1902, 35, 4409).
8 : 3 : 4 : 9 Needles: *lactone*, needles, m.p. 160° (Pschorr and Popovici, Ber. 1906, 39, 3120).

(vi) **Trimethoxyphenanthrenecarboxylic acids**, [OMe : OMe : OMe : CO_2H].
3 : 4 : 5 : 9 Prisms, m.p. 234°-235° (Pschorr, Zeidler and Dickhäuser, Annalen, 1912, 391, 47; Pschorr and Koch, *ibid.* 58).

3 : 4 : 6 : 8 Needles, m.p. 201°; *methyl* ester, needles, m.p. 101°-102°; *ethyl* ester, leaflets, m.p. 83°-84° (Knorr and Pschorr, Ber. 1905, 38, 3158; Pschorr and Rettberg, Annalen, 1910, 373, 51).
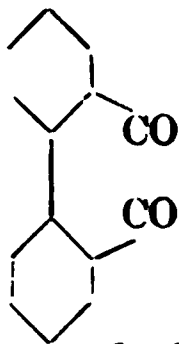3 : 4 : 6 : 9 Yellow needles, m.p. 203° (Pschorr, Seydel and Stöhrer, Ber. 1902, 35, 4406).
3 : 4 : 7 : 9 Needles, m.p. 214° (Pschorr, Zeidler and Dickhäuser, *l.c.*).
3 : 4 : 8 : 5 Needles, m.p. 224°-226° (Pschorr and Massaciu, Ber. 1904, 37, 2790; Pschorr and Loewen, Annalen, 1910, 373, 70). The 8-*ethoxy* acid forms needles, m.p. 191°.
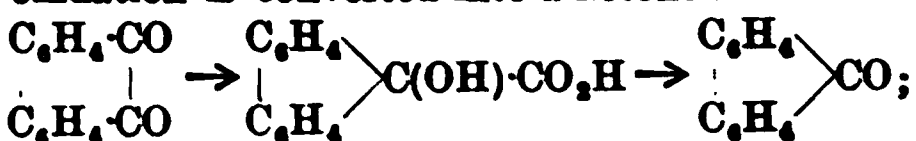3 : 4 : 8 : 9 Leaflets, m.p. 250° (Pschorr and Busch, Ber. 1907, 40, 2003). The 8-*ethoxy* acid forms leaflets, m.p. 265° (Pschorr and Zeidler, Annalen, 1910, 373, 78).
(vii).3 : 4-**Dimethoxy-5 : 6-methylenedioxyphenanthrene-8-carboxylic acid**, needles, m.p. 228° (Gadamer and Kuntze, Arch. Pharm. 1911, 249, 630).

DIHYDROPHENANTHRENE DERIVATIVES.

Phenanthraquinone is a typical member of the series of *ortho*-quinones, but unlike [β-]naphthaquinone, to which it shows a close resemblance in properties, it can be obtained from the corresponding hydrocarbon by direct oxidation. It gives the characteristic reactions of an *ortho*-diketone, as may be seen by comparison with benzil; thus it reacts with hot caustic alkali solution, forming a glycollic acid, which by oxidation is converted into a ketone:

$$\begin{array}{c}C_6H_4\text{·}CO \\ | \\ C_6H_4\text{·}CO\end{array} \rightarrow \begin{array}{c}C_6H_4 \\ \diagdown \\ C_6H_4 \diagup\end{array}\!\!C(OH)\text{·}CO_2H \rightarrow \begin{array}{c}C_6H_4 \\ \diagdown \\ C_6H_4 \diagup\end{array}\!\!CO;$$

yields azines by condensation with *ortho*-diamines; and gives a mono- and a di-oxime with hydroxylamine. The relationship between the colour and constitution of the dioxime and its derivatives has been discussed by Schmidt and Söll (Ber. 1907, 40, 2454; *cf.* Hantzsch and Glover, *ibid.* 4344; Schmidt and Mezger, *ibid.* 4560).

Substitution derivatives of phenanthraquinone are formed either by oxidising the corresponding phenanthrene derivatives (other than 9-, 10-, or 9 : 10- compounds), or by direct substitution. In the latter case substitution usually occurs in the equivalent 2- and 7- positions, thus recalling the formation of *meta*-derivatives of benzene under the directing influence of the carbonyl radicle.

Preparation.—Crude phenanthrene (100 grams), consisting of the easily soluble constituents of the coal-tar fraction boiling at 320°-340°, is warmed with a solution of potassium dichromate (300 grams) in sulphuric acid (900 grams), diluted with water (1·5 litres), and, after the vigorous reaction has subsided, more dichromate (300 grams) is added gradually, the liquid finally being boiled for some time. After precipitation by water the quinone is washed, dried, stirred into concentrated sulphuric acid, and after 24 hours mixed with water. Chromium salts, diphenic acid, acridine, &c., pass into solution, the last traces of organic acids or hydrocarbons being removed by extracting the residue with cold, dilute caustic soda solution, and afterwards (when dry) with ether. The residue is freed from anthraquinone by digestion with warm concentrated sodium bisulphite solution in which the phenanthraquinone dissolves, and the filtrate poured into a solution of potassium dichromate in dilute sulphuric acid;

p-nitrophenetole gradually to a solution of 848 grams of stannous chloride in 1060 of hydrochloric acid at 50°-60°. It is then precipitated from solution as the hydrochloride by the addition of concentrated hydrochloric acid (Paul, Zeitsch. angew. Chem. 1896, 587).

p-Phenetidine may also be prepared by treating *p*-azophenetole with tin and hydrochloric acid (D. R. P. 48543); or by heating benzylidene-*p*-aminophenol with ethyl bromide and alcoholic sodium hydroxide for 3 hours. The product is then warmed with acid when *p*-phenetidine separates (D. R. P. 69006).

p-Phenetidine is a liquid, b.p. 254·2°-254·7°, m.p. 2·4° (Schneider, Zeitsch. physikal. Chem. 1896, 19, 155). When heated with hydrogen peroxide and dilute sulphuric acid, it yields a brown colouring matter $C_{24}H_{22}N_2O_5$, but when oxidised in the cold with a permanganate it yields quinone, carbon dioxide, acetic and oxalic acids, and resinous substances (Kinzel, Arch. Pharm. 229, 329). When to an alcoholic solution, 5 c.c. of a potassium iodide solution are added and the mixture is heated, a rose-red colour is formed (Goldmann, Pharm. Zeit. 1893, 36, 208). For the detection of phenetidine in urine *see* Edlefsen, Chem. Zentr. 1900, i. 573.

p-Phenetidine sulphonic acid is prepared by heating the hydrogen sulphate of the base or by boiling *p*-nitrophenetole with sodium hydrogen sulphite. It forms readily crystalline sodium salts, and may be diazotised and joined with *β*-naphthol, thus obtaining the azo- compounds which with barium and aluminium hydroxides form red lakes of great brilliancy and fastness (D. R. P. 146655; *see* also D. R. P. 189469). *p*-Phenetidine sulphonic acid may also be obtained by heating phenetidine with fuming sulphuric acid (Eng. Pat. 14375, 1897; *see* also Cohn, Annalen, 1899, 309, 234; Paul, *l.c.*).

Ethyl sulphone phenetidine

$$EtO \cdot C_6H_4 \cdot NHSO_2 \cdot C_2H_5$$

is obtained by the action of ethyl sulphochlorides on *p*-phenetidine. It forms shining white leaflets, m.p. 80°-81°, and acts as a monobasic acid, forming well-crystallised salts which may be employed in medicine as they have antineuralgic, antipyretic, sedative and hypnotic properties (Autenrieth and Bernheim, Arch. Pharm. 1904, 242, 579). Similar aromatic sulpho derivatives, also employed in medicine, have been prepared (Eng. Pat. 3791, 1896).

By the interaction of *p*-phenetidine and its homologues with ethyl orthoformate, compounds are formed of the type of methenyldi-*p*-phenetidine, which possess anæsthetic properties (Goldschmidt, Chem. Zeit. 1902, 26, 745; J. Soc. Chem. Ind. 1890, 650).

The following derivatives of *p*-phenetidine also have medicinal properties :—

The *citrates*, *tartrates*, and *mandelates* prepared by mixing the theoretical quantities of the acid and base dissolved in suitable solvents (Eng. Pat. 11288, 1895).

Lactyl-p-phenetidine (*lactophenin*) is prepared by heating benzylidene *p*-phenetidine with lactic acid (Eng. Pat. 19188, 1894; *see* also Eng. Pat. 29869, 1895). It forms colourless prisms. The *diacetate* of *p*-phenetidine, m.p. 55°-56°, b.p. 182° /12 mm. is obtained by heating phenacetin (p-*phenetidine monoacetate*) with a large excess of acetic anhydride (D. R. P. 75611; Bistrzycki and Ulffers, Ber. 1898, 31, 2788; Cohn, *ibid.* 1899, 32, 2239). *Benzyl-p-phenetidine*, m.p. 45°-46°, obtained by heating benzyl chloride with *p*-phenetidine forms crystalline plates (Wenghöffer, Chem. Zeit. 19, 1753; Wedekind and Fröhlich, Ber. 1907, 40, 1001). *Ethoxyphenyloxamide* $(CO)_2(NH \cdot C_6H_4 \cdot OEt)_2$ by heating anhydrous oxalic acid with *p*-phenetidine to 140°-145°. It forms thin needles, m.p. 263° (Wenghöffer, *l.c.*).

Amygdalyl phenetidine by heating *p*-phenetidine mandelate to 170°, forms shining white plates, m.p. 140·5° (Wenghöffer, *l.c.*). *Ethyl β-pheneldyl crotonate* obtained by condensing *p*-phenetidine with ethyl acetoacetate, forms, when heated rapidly, to 225°-240°, p-*ethoxy-γ-hydroxyquinaldine* $EtOC_6H_3 \cdot NCCH_3 \cdot C(OH) \cdot CH$, which has powerful antipyretic properties (Wenghöffer, *l.c.*). *Salicyl - p - phenetidene* (*Saliphen*), m.p. 142°-143°, is prepared by heating the constituents with phosphorus oxychloride; its *aceto* derivative has m.p. 92° (U.S. Pats. 706355, 706356, 1902; Bolezzi, Gazz. chim. ital. 1898, 28, ii. 197). Also *amino acet-p-phenetidine* (*Phenocoll*), *valeryl-p-phenetidine* (*Sedatin*), *vanillin*-p-*phenetidine*, and the *furfural, propionyl, methyl glycolic*, and *acetosulphonic* derivatives (J. Soc. Chem. Ind. 1898, 726; Eng. Pat. 14954, 1896; 4565, 1905).

For the *halogen* derivatives, *see* Staedel (Annalen, 1883, 217, 55); Reverdin (Ber. 1896, 29, 2595); Reverdin and Düring (*ibid.* 1899, 32, 152); Grothe (Arch. Pharm. 1900, 238, 587, 600). Nitro derivatives are described by Wender (Gazz. chim. ital. 19, 218); Autenreith and Hinsberg (Arch. Pharm. 229, 456); Blanksma (Rec. trav. chim. 1905, 24, 40).

For other derivatives, *see* Boettinger (Arch. Pharm. 1896, 234, 158); Wirths (*ibid.* 620); Meves (J. pr. Chem. 1900, [ii.] 61, 449); Vorländer (Annalen, 1897, 294, 273, 302); Bischoff (Ber. 1898, 31, 3241, 3248); Partheil and Schumacher (*ibid.* 591); Sachs and Levy (*ibid.* 1904, 37, 874); Schroeter (*ibid.* 1905, 38, 3181); Bischoff and Fröhlich (*ibid.* 1906, 39, 3976); Erlenmeyer (*ibid.* 791); Goldschmidt (Chem. Zeit. 1901, 25, 178); Lumière and Barbier (Bull. Soc. chim. 1906, [iii.] 35, 123); Fourneau (J. Pharm. Chim. 1910, [vii.] 1, 97).
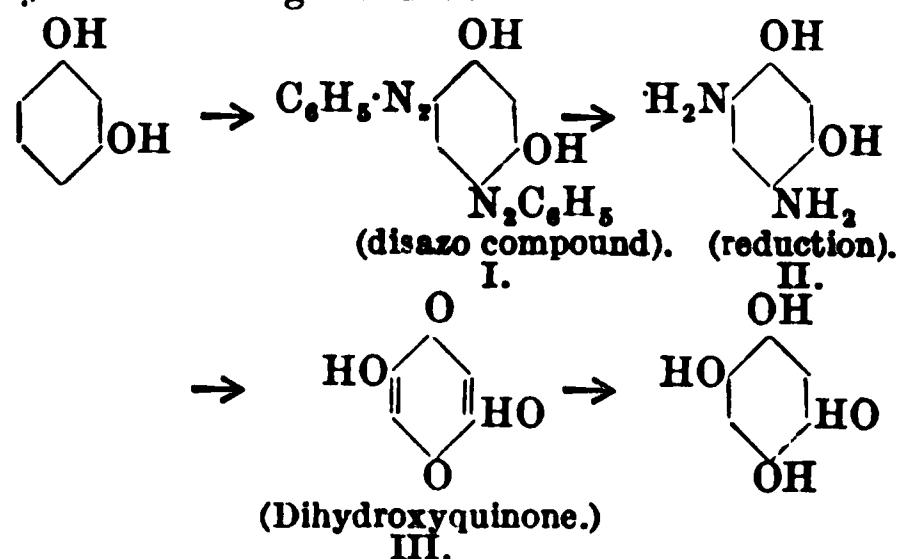
o-Phenetidine is produced as a by-product in the formation of the para- compound.

PHENETOLE $C_6H_5 \cdot O \cdot C_2H_5$.

Preparation. —Phenetole can be obtained by heating potassium phenate with ethyl iodide (Cahours, Ann. Chim. Phys. [iii.] 27; 463), or by heating a mixture of equal parts of phenol and phosphorus pentoxide at 200° and gradually adding alcohol (Kastropp, Ber. 1877, 10, 1685). It is prepared by heating molecular proportions of crude calcium or sodium sulphovinate and sodium phenate (prepared by mixing molecular proportions of phenol and aqueous caustic soda of sp.gr. 1·33) at 150° for some hours (Kolbe, J. pr. Chem. [ii.] 27, 424).
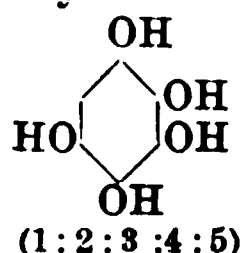
It may also be prepared by fusing perfectly dry sodium ethoxide with perfectly dry phenyl sulphonate (Mouren, J. Pharm. Chim. 1898, 8, 211); by the action of sodium ethoxide on triphenyl phosphate (Morel, Compt. rend. 1899, 128, 508); or by passing alcohol into a mixture of

from resorcinol in a manner which is indicated by the following scheme :—

OH
⬡OH → $C_6H_5 \cdot N_2$ ⬡OH → H_2N ⬡OH
    $N_2C_6H_5$ NH_2
    (disazo compound).   (reduction).
    I.   II.

→ HO⬡HO → HO⬡HO
    O   OH
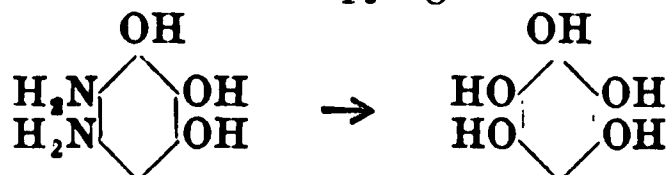   (Dihydroxyquinone.)
    III.

sym-Resorcinoldisazobenzene (I.) is formed by the action of benzene diazonium chloride on resorcinol in the presence of excess of caustic alkali. This is reduced to diaminoresorcinol (II.), which yields diiminoresorcinol on oxidation, a substance which is converted into dihydroxyquinone (III.) on treatment with caustic alkali; the last-named compound is reduced to the tetrahydric phenol by stannous chloride. The tetrahydroxybenzene forms glistening leaflets which melt between 215° and 220°; the aqueous solution becomes rapidly brown on exposure to the air and is at once oxidised to dihydroxyquinone by ferric chloride.

Pentahydric phenol. There is only one theoretically possible pentahydroxy derivative of benzene, namely—

OH
⬡OH
HO⬡OH
OH
(1 : 2 : 3 : 4 : 5)

1 : 2 : 3 : 4 : 5-*Pentahydroxybenzene*. A substance having this constitution has been described by Wenzel and Weidel (Chem. Zentr. 1903 [ii.] 829) as forming colourless crystals insoluble in all the usual organic solvents. Different properties are given to this compound by Einhorn, Coblinger and Pfeiffer (Ber. 1904, 37, 122), who prepared it by the action of water on the hydrochloride of 4 : 6-diaminopyrogallol

OH   OH
H_2N⬡OH → HO⬡OH
H_2N⬡OH   HO⬡OH

It forms microscopic needles when crystallised from benzene which are readily soluble in ether, alcohol, or ethyl acetate, and which blacken when heated. The aqueous solution gives a dark-red brown colour with ferric chloride. The *penta-acetyl* derivative forms colourless needles which melt with decomposition at 165°.

The only *hexahydric phenol*, hexahydroxybenzene $C_6(OH)_6$, has been prepared by Nietzki and Benckiser (Ber. 1885, 18, 499, 1833) from the diacetyl derivative of hydroquinone in the following way—

O
OAc   ‖   OH
⬡ → O_2N⬡-OH → H_2N⬡OH
HO-   NO₂   HO   NH.
OAc   ‖   OH
O
(I.)   (II.)

CO   OH
→ CO⬡CO → HO⬡OH
    CO⬡CO   HO⬡OH
    CO   OH
    (III.)   (IV.)

The diacetyl derivative is converted into the so-called 'nitranilic acid' (I.) by the action of nitric and sulphuric acids; this is then reduced to diaminotetrahydroxybenzene (II.) which is oxidised by means of nitric acid to triquinoyl (III.); the latter is then reduced by stannous chloride to hexahydroxybenzene (IV.). The hexahydric phenol forms long needles which cannot be obtained completely colourless; when heated it becomes dark-grey at about 200° without melting. It is sparingly soluble in cold water, but readily dissolves on warming, and is sparingly soluble in alcohol, ether, or benzene. The aqueous solution becomes quickly red-violet on exposure to the air and at once reduces silver nitrate. It is oxidised by concentrated nitric acid to triquinoyl and when its alkaline solution is treated with air, it is converted into tetrahydroxyquinone. The action of dilute alkali yields potassium croconate, and acetic anhydride produces the *hexa-acetyl* derivative which melts at 203° (Maquenne, Bull. Soc. chim. 1887, 48, 64). The potassium salt of hexahydroxybenzene is identical with 'kohlenoxydkalium,' which is prepared by the action of dry carbon monoxide on melted potassium (Gmelin, Pogg. Ann. 1825, 4, 35). J. F. T.

PHENOL COLOURING MATTERS *v.* OXAZINE COLOURING MATTERS.

PHENOL CORALLIN *v.* AURIN.

PHENOLPHTHALEÏN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHENOPHENANTHRAZINE *v.* AZINES.
PHENOSAFRANINE *v.* AZINES.
PHENOSAL *v.* SYNTHETIC DRUGS.
PHENYFORM *v.* SYNTHETIC DRUGS.

PHENYL. Under this heading will be described the monosubstituted derivatives of benzene, having the general formula C_6H_5R. The radicle C_6H_5 is known as phenyl and is monovalent.

Aminobenzene *v.* ANILINE.

Bromobenzene, *Phenyl bromide* C_6H_5Br. Prepared by the interaction of benzene and bromine in the presence of sunlight (Schramm. Ber. 1885, 18, 606), iodine (Rilliet and Ador, *ibid.* 1875, 8, 1287), aluminium chloride (Leroy, Bull. Soc. chim. 1887, 48, 211 ; Greene, Compt. rend. 90, 40), or aluminium amalgam (Cohen and Dakin, Chem. Soc. Trans. 1899, 894); by the action of phenylhydrazine on perbromacetone (Levy and Jedlicka, Annalen, 249, 84); by the action of sulphur bromide and nitric acid on benzene (Edinger and Goldberg, Ber. 1900, 33, 2884); by diazotising aniline in the presence of copper, sulphuric acid, and potassium bromide (Sandmeyer. *ibid.* 1884. 17, 2650); for electrolytic method *v.* Votoček and Zeníšek (Chem. Zentr. 1899, i. 1146).

Bromobenzene is a colourless liquid, b.p. 156·6° (758·6 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 70); m.p. −30·5° (corr.) (Schneider, *ibid.* 22, 232 ; *cf.* Haase, Ber. 1893, 26, 1053); sp.gr. 4°/4° 1·5105, 15°/15° 1·4991. 25°/25° 1·4886, 50°/50° 1·4681, 100°/100° 1·4416; magnetic

rotation (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Ramsay and Young, *ibid.* 1885, 646, 655; Young. *ibid.* 1889, 488, 506; Kahlbaum, Zeitsch. physikal. Chem. 26, 584); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 811); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 386). Heated with aluminium chloride, bromobenzene yields benzene and isomeric dibromobenzenes (Dumreicher, Ber. 1882, 15, 1867); with sodium methoxide at 200° anisole, phenol, and a small quantity of benzene are formed (Blau, Monatsh. 7, 626). Sodium in ether yields hydrocarbons of high molecular weight and a dark-blue substance (Weiler, Ber. 1896, 29, 115; Mohr, J. pr. Chem. 1909, [ii.] 80, 315); ethyl oxalate and sodium in absolute ether yield benzoic acid and triphenylcarbinol (Frey, Ber. 1895, 28, 2315). Heated with sulphuric acid, bromobenzene yields 1 : 3 : 5-dibromobenzene sulphonic acid and a bromobenzene disulphonic acid (Herzig, Monatsh 2, 192); nitric acid (sp.gr. 1·5) gives 1 : 2 : 4-bromodinitrobenzene together with *o*- and *p*-bromonitrobenzenes (Bandrowski, Bull. Acad. Sci. Cracow, 1900, 193). Hydriodic acid and phosphorus are without action on bromobenzene at 218° (Klages and Liecke, J. pr. Chem. [ii.] 61, 319).

Chlorobenzene, *Phenyl chloride,* C_6H_5Cl. Prepared by the action of phosphorus pentachloride on phenol (Gerhardt and Laurent, Annalen, 75, 79); by heating benzene with thionyl chloride at 150° (Dubois. Zeitsch. Chem. 1866, 705) or with sulphur chloride at 250° (Schmidt, Ber. 1878, 11, 1173); by the electrolysis of a strong hydrochloric acid solution of cupric chloride in the presence of benzene diazonium chloride using copper electrodes (Votoček and Zeniśek, Chem. Zentr. 1899, i. 1146; *cf.* Walter, J. pr. Chem. 1896, [ii.] 53, 427); by diazotising aniline and heating the product with cuprous chloride (Sandmeyer, Ber. 1884, 17, 1633); by the action of chlorine on benzene in the presence of aluminium chloride (Mouneyrat and Pouret, Compt. rend. 1898, 127, 1026), ferric chloride (Thomas, *ibid.* 1898, 126, 1212), or a mixture of finely divided iron and ferric chloride (D. R. P. 219242; J. Soc. Chem. Ind. 1910, 619).

Chlorobenzene is a colourless liquid, b.p. 131·8° (757 mm.) (Perkin, Chem. Soc. Trans. 1896, 387; *cf.* Ramsay and Young, *ibid.* 1885, 642, 654; Fuchs. Zeitsch, angew. Chem. 1898, 869); m.p. −45° (corr.) (Schneider, Zeitsch. physikal. Chem. 19, 155); sp.gr. 4° 4° 1·1230, 15°/15° 1·1125, 25° 25° 1·1042, 50° 50° 1·0868, 100°/100° 1·0623 (Perkin, *l.c.*); critical temperature 359·2° (Young. Zeitsch. physikal. Chem. 11, 590; Schneider, *ibid.* 70, 626); vapour pressure (Young. Chem. Soc. Trans. 1889, 90, *et seq.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911. 811); magnetic rotation (Perkin, *l.c.*); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 387). By passing the vapour of chlorobenzene over red-hot iron filings, diphenyl, mono- and di- chlorodiphenyl and diphenylbenzene are formed (Kramers, Annalen, 189, 135). On heating with sodium in carbon tetrachloride, triphenylmethane, hexaphenylbenzene and diphenyl are produced

(Schmidlin, Compt. rend. 1903, 137, 59), whilst with aluminium chloride the products are the chlorides of 4 : 4'- and 2 : 4'-dichlorobenzophenones (Norris and Green. Amer. Chem. J. 1901, 26, 492; Norris and Tweig, *ibid.* 1903, 30, 392). Chlorine in the sunlight yields $C_6H_5Cl.Cl_4$, $C_6H_4Cl_2$, and other products; in the presence of dilute sodium hydroxide, *a*- and β-chlorobenzene hexachlorides are produced (Matthews, Chem. Soc. Trans. 1891, 167; 1892, 103). Bromine in the presence of aluminium chloride yields *p*-chlorobromobenzene and other products (Mouneyrat and Pouret, Compt. rend. 1899, 129. 605); sulphuric acid and iodine yield chlorodiiodobenzene (Cl : I_2 = 1 : 2 : 4), chlorotriiodobenzene (Cl : I_3 = 1 : 2 : 4 : 6) and other products (Istrati, Chem. Zentr. 1897, i. 1161). Chlorobenzene remains unchanged on heating with hydriodic acid and phosphorus at 302° (Klages and Liecki, J. pr. Chem. [ii.] 61, 319). Nitric acid at 0° gives *o*-, *m*-, and *p*-chloronitrobenzenes, the yields being 29·8, 0·3 and 69·9 p.c. respectively (Holleman, Proc. K. Akad. Wetensch. Amsterdam, 1905, 7, 266). Oxidised by sulphuric acid and manganese dioxide to formic and *p*-chlorobenzoic acids. Has been recommended as a solvent for resins (Andès, Chem. Rev. Fett. Harz-Ind. 1906, 13, 32). For stability of halogenated benzenes *v.* Löwenherz (Zeitsch. physikal. Chem. 1899, 29, 401); Vandevelde (Chem. Zentr. 1898, i. 438).

Iodobenzene, *Phenyl iodide,* C_6H_5I. Prepared by the action of phosphorus triiodide on phenol (Scrugham, Annalen, 92, 318); by heating a mixture of benzene and iodine with aluminium chloride (Green, Compt. rend. 90, 40), ferric chloride (Meyer, Annalen, 231, 195), or with sulphuric acid (Neumann, *ibid.* 241, 84; Istrati and Georgescu, Chem. Zentr. 1892, i. 625), in the last method higher halogenated compounds also being formed; by the interaction of benzene and sulphur iodide in the presence of nitric acid (Edinger and Goldberg, Ber. 1900, 33, 2876); by heating phenyl hydrazine with excess of iodine in potassium iodide solution (Meyer, J. pr. Chem. [ii.] 36, 115); by heating benzene with potassium iodate and dilute sulphuric acid (Peltzer, Annalen, 136, 197); by heating sodium benzoate with iodine monochloride (Schützenberger, J. 1861, 349; 1862, 251).

Iodobenzene is a colourless liquid, b.p. 188·36° (755·75 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 71); m.p. −28·5° (corr.) (Schneider, *ibid.* 19, 157; *cf.* Haase, Ber. 1893, 26, 1053); sp.gr. 4° 4° 1·8551, 15° 15° 1·8401, 25°/25° 1·8283, 50° 50° 1·8067, 100° 100° 1·7832 (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Young. *ibid.* 1889, 490, 510); heat of combustion 770·0 Cal. (Berthelot, Compt. rend. 130, 1098); magnetic rotation (Perkin, *l.c.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911. 2318). Iodobenzene is reduced to benzene by sodium amalgam in alcohol; with aluminium chloride it yields benzene, isomeric diiodobenzenes, hydrochloric acid and iodine (Dumreicher, Ber. 1882, 15, 1808); with silver nitrate at 145° picric acid is formed (Geuther, Annalen, 245, 100); oxidised by Caro's acid to iodoxybenzene (Bamberger and Will, Ber. 1900, 33, 534).

PHENYLACETIC ACID.

Homogentisic acid has been synthesised by heating quinol dimethyl ether dissolved in carbon disulphide with ethylchloracetate and aluminium chloride, and subsequent hydrolysis with red phosphorus and fuming hydriodic acid of the methyl ether of homogentisic acid thus obtained (Osborne, Proc. Physiol. Soc. 1903, 13, 14).

Homogentisic acid forms prisms that melt at 146·5°–147°, and pass into the *lactone*

$$OH \cdot C_6H_3 \underset{CH_2}{\overset{O}{<}} CO,$$

m.p. 191°. The *lead salt* $Pb(C_8H_7O_4)_2, 3H_2O$ has m.p. 214°–215°, is soluble in 675 parts of water at 20°, and advantage is taken of this sparing solubility in the isolation of the acid. The *ethyl ester* has m.p. 119°–120°; the *dimethyl ether* $(OMe)_2C_6H_3 \cdot CH_2 \cdot CO_2H$ has m.p. 124·5°; and its *methyl ester* $(OMe)_2C_6H_3 \cdot CH_2 \cdot CO_2Me$, m.p. 45° (Wolkow and Baumann, Zeitsch. physiol. Chem. 1894, 15, 228; Baumann and Fränkl, ibid. 20, 221). *Dibenzoylhomogentis-amide* has m.p. 204° (Orton and Garrod, J. Physiol. 1901, 27, 89). Homogentisic acid reduces copper and silver salts readily, gives a blue colour with ferric chloride, and yields gentisic acid (2 : 5-dihydroxybenzoic acid) and quinol on fusion with potassium hydroxide at 195°–196°. For the chemistry of the colour reactions afforded by homogentisic acid with amines, see Mörner, Zeitsch. physiol. Chem. 1910, 69, 329.

Estimation.—Homogentisic acid in urine is estimated by measuring its reducing action on silver nitrate. 10 c.c. of the filtered urine, 10 c.c. of ammonia solution (8 p.c.), 20 c.c. of N/10 silver nitrate solution are placed in a flask, after five minutes 5 drops of calcium chloride and 10 drops of ammonium carbonate solution are added, the solution made up to 50 c.c., and the silver estimated in half the filtrate. One molecule of homogentisic acid reduces 4 atoms of silver (Baumann, Zeitsch. physiol. Chem. 1895, 16, 268; Denigès, J. Pharm Chem. 1897, [vi.] 5, 50; Garrod and Hurtley, J. Physiol. 1905, 33, 206).

PHENYLALANINE, *β-phenyl-α-aminopro-pionic acid, α-aminohydrocinnamic acid*

$$C_6H_5 \cdot CH_2 \cdot CH(NH_2)CO_2H$$

was discovered in the etiolated seedlings of *Lupinus luteus* (Schulze and Barbieri, Ber. 1879, 12, 1924; 1881, 14, 1785), and occurs in many other germinating plants (Schulze, Zeitsch. physiol. Chem. 1888, 12, 405; 1892, 17, 193; 1894, 20, 306; 1896, 22, 411; 1900, 30, 241). Winterstein (ibid. 1904, 41, 485) found it among other products of proteid hydrolysis in Emmen-thaler cheese; and Abderhalden and Barker (ibid. 1904, 42, 524) showed that it occurs in the urine of dogs suffering from phosphorus poisoning.

The naturally occurring phenylalanine (*l*-phenylalanine) originates from the protein of the germinating plant, and it can also be readily obtained by the hydrolysis of a large number of proteids (v. PROTEINS) by means of hydrochloric acid, stannous chloride, or baryta (Schulze and Barbieri, Ber. 1883, 16, 1711; Zeitsch. physiol. Chem. 1884, 9, 63); it occurs in that fraction of the esterified products of hydrolysis that boils at 130°–190° 0·5 mm., and is isolated by precipitation from the mixed esters by means of water (Fischer, ibid. 1901, 33, 412),

or by means of its sparingly soluble copper salt (Schulze and Barbieri, J. pr. Chem. 1883, [ii.] 27, 337; compare Schulze and Winterstein, Ber. 1902, 35, 210).

Synthesis.—The constitution of phenylalanine was determined by Erlenmeyer and Lipp (Ber. 1882, 15, 1006), who synthesised it from phenyl-acetaldehyde, hydrogen cyanide, and ammonia

$$C_6H_5 \cdot CH_2 \cdot CHO \rightarrow C_6H_5 \cdot CH_2 \cdot CH(NH_2)CN$$
$$\rightarrow C_6H_5 \cdot CH_2 \cdot CH(NH_2)CO_2H.$$

Plöchl (ibid. 1883, 16, 2815; 1884, 17, 1616) obtained it by the reduction and subsequent hydrolysis of α-benzoylaminocinnamic acid obtained by the condensation of benzaldehyde with hippuric acid in the presence of acetic anhydride—

$$C_6H_5 \cdot CHO + CH_2(NH \cdot COPh)CO_2H$$
$$\rightarrow C_6H_5 \cdot CH : C(NH \cdot COPh)CO_2H$$
$$\rightarrow C_6H_5 \cdot CH_2 \cdot CH(NH \cdot COPh)CO_2H$$
$$\rightarrow C_6H_5 \cdot CH_2 \cdot CH(NH_2)CO_2H.$$

For a complete explanation of the mechanism of this reaction which is more complex than indicated above, see Erlenmeyer (Annalen, 1893, 275, 1, 13); and Erlenmeyer and Kunlin (ibid. 1899, 307, 146).

For the preparation of synthetic phenyl-alanine Fischer's method is the most practical (Ber. 1904, 37, 3062). It consists in the preparation of the corresponding bromo-fatty acid starting with ethyl malonate and benzyl chloride, and treating this with ammonia—

$$(CO_2Et)_2CH_2 \rightarrow (CO_2Et)_2CH \cdot CH_2 \cdot C_6H_5$$
$$\rightarrow (CO_2H)_2CH \cdot CH_2 \cdot C_6H_5$$
$$\rightarrow (CO_2H)_2CBr \cdot CH_2 \cdot C_6H_5$$
$$\rightarrow CO_2H \cdot CHBr \cdot CH_2 \cdot C_6H_5$$
$$\rightarrow CO_2H \cdot CH(NH_2)CH_2 \cdot C_6H_5.$$

For other methods of synthesis, see Sörensen (Zeitsch. physiol. Chem. 1905, 44, 448); Wheeler and Hoffman (Amer. Chem. J. 1911, 45, 368).

The phenylalanine obtained by any of the synthetic processes described above is the racemic (*dl*-) form, it can be resolved into its optically active isomerides by the fractional crystallisation of the cinchonine salt of the benzoyl derivative (Fischer and Mouneyrat, Ber. 1900, 33, 2383), or the brucine salt of the formyl derivative (Fischer and Schoeller, Annalen, 1907, 357, 1). *d*-Phenylalanine can be obtained by the selective action of yeast in a sucrose solution on *dl*-phenylalanine (Ehrlich, Biochem. Zeitsch. 1908, 8, 438).

l-**Phenylalanine** crystallises in anhydrous shining plates or hydrated needles containing 4 p.c. water (Schulze and Winterstein, l.c.), soluble in 32·4 parts of water at 25°, m.p. 275° (corr.) with decomposition, $[a]_D^{20} -35\cdot1°$, and has a slightly bitter taste (Fischer and Schoeller, l.c.). The *copper salt* $(C_9H_{10}O_2N)_2Cu$ is almost insoluble in water; the *hydrochloride*

$$C_9H_{11}O_2N, HCl$$

and hydrobromide are crystalline and stable; the *ethyl ester* $C_9H_{10}N \cdot CO_2Et$ is an oil and forms a crystalline hydrochloride $C_9H_{10}N \cdot CO_2Et, HCl$, $[a]_D^{20} -7\cdot6°$; the *formyl* derivative forms sharp four-sided plates, m.p. 167° (corr.), and has $[a]_D^{20} +75\cdot2°$; the *brucine* salt crystallises in warty masses from methyl alcohol; the *benzoyl*

(d) *Concentration of phosphoric acid liquor from the filters.* This may be accomplished either in shallow rectangular wooden tanks, lined with 10 lbs. lead, and provided with lead pipes (1½ in. diameter, and 20 lbs. lead to 1 ft.) through which high-pressure steam is allowed to pass; or it may be performed in a cast-iron saucer-shaped pan, also lined with lead and having steam coils as before. During evaporation the liquor is maintained in motion by an agitator, provided with arms, and driven as usual by power. The latter system is the one to be preferred. Agitation of the liquor during concentration, besides hastening the evaporation, prevents the accumulation of gypsum on the steam coils, a result which invariably occurs in any unstirred evaporator. Such deposit, if allowed to form, becomes extremely hard and difficult to remove without injury to the lead pipes.

The stronger phosphoric acid from the filters

—that above 10°Twad.—is allowed to flow by gravitation from the stock tank to the evaporator, to be concentrated till the clear yellow-coloured phosphoric acid attains a strength of from 65°Twad. to 100°Twad. (sp.gr. 1·325 to 1·500), according—as will be immediately explained—to the selected method of subsequent treatment. During the evaporation nearly all the calcium sulphate held in solution is precipitated, so that the concentrated acid liquor retains only a very small quantity of lime. Almost all of this lime ultimately deposits as sulphate after settling in the stock tank. As the phosphoric acid liquor becomes more and more concentrated, some of the free sulphuric acid which may be present is expelled during the evaporation—the steam or vapour from the evaporator having frequently a strong acid reaction. The following are some analyses of phosphoric acid liquors at various strengths made from phosphates which are not named :—

	Strength				
	58°T.	69°T.	72°T.	86°T.	90°T.
Uncombined phosphoric acid (P₂O₅)	19·30	27·60	29·20	34·02	36·44
Combined phosphoric acid (P₂O₅)	4·68	3·61	3·60	4·40	4·80
Sulphuric acid (SO₃)	2·47	1·40	0·70	—	1·39
Alumina and ferric oxide, &c.	1·92	2·56	—	3·26	3·61
Lime	—	1·00	—?	0·84	trace
Water	71·63	63·83	66·50	57·48	53·76
	100·00	100·00	100·00	100·00	100·00

The gypsum deposited in the evaporators or in the stock tank may either be washed by itself on a small filter, or it may be removed to the large acid filter, and be washed along with the sludge from the decomposer. If conveniently situated, the latter is the more economical method.

The concentrated acid is cooled in lead-lined store tanks, where, as has been said, the last traces of calcium sulphate are deposited, and the acid is then ready for the next operation of mixing with carbon and drying.

(e) *Mixture for the retorts.* The concentrated phosphoric acid may now be mixed with coarsely-ground wood charcoal, coke, or sawdust, and carefully dried in a cast-iron pot or muffle furnace. Sawdust absorbs a large quantity of liquor, so that when it is employed concentration of the acid liquor to the minimum sp.gr. of 1·320 is permissible, and, when thus saturated, it can be easily handled without loss through sweating.

On the other hand, its greater bulk and low specific gravity present objectionable features. If sawdust be employed, the mixing may be accomplished on a clean brick or asphalt floor and the wet charge can then be carefully charred in a well-built muffle furnace.

If coke or charcoal be used, the preliminary concentration of the phosphoric acid to a syrupy consistence is indispensable, and the mixing should be done in a cast-iron pot, in which the charge is subsequently dried by fire-heat from beneath. The amount of fixed carbon required is about 25 p.c. by weight of the concentrated

acid liquor. Great care must be taken with the drying of the charge. The heat must be regular and not too high, and when it is completed the charred mass must be carefully preserved from air in malleable or cast-iron boxes provided with closely-fitting lids, and conveniently situated for the retorts.

(f) *The description of the clay retorts, their manufacture, and details of the clay employed.* The retorts in which the charred mixture is distilled are made of Stourbridge fireclay. The retorts are shaped much like a large bottle. The accompanying sectional sketch will show the appearance they present.
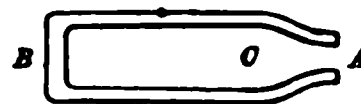

FIG. 1.—PHOSPHORUS RETORT MADE OF STOURBRIDGE CLAY.

The total length A to B is 3 ft. The internal diameter is about 8 ins. The clay is about 1 in. thick, except at B, where it is about 1½ ins. The neck is gradually tapered from C to A, where the internal diameter is 3 ins. Into this narrow orifice a 2-inch mal. iron pipe leading to the condenser is luted, and can be easily removed to empty and charge the retorts.

The retorts should be made at the phosphorus works; the clay employed is such as is used for glass-house pots, and is tolerably free from iron, rich in silica, and comparatively low in alumina. The clay, as generally supplied from Stourbridge, has previously undergone the operation of 'weathering' for many months.

Stock and Johannsen, *ibid.* 1908, 41, 1593). It varies in colour from pure white to dark red, according to the time of heating in its preparation and has sp.gr. of 2·51 at 18°. At the ordinary temperature it is inactive, but acts as a powerful reducing agent at a high temperature. It is decomposed by many metals and by water at 180°. When heated in chlorine or oxygen it takes fire.

Phospham $PN_2H(?)$ is obtained as an amorphous, light, white powder, insoluble in water and infusible at a red heat, when the product of the reaction of ammonia on phosphorus pentachloride is heated in the absence of air until fumes of ammonium chloride cease to be evolved (Besson, Compt. rend. 1892, 114, 1264; Besson and Rosset, *ibid.* 1908, 146, 1149). When dry, it is oxidised by heating in air, evolving white fumes; if previously moistened it decomposes thus:

$$3PHN_2 + 9H_2O = 3HPO_3 + 6NH_3.$$

Phosphoramide $P(NH_2)_3$ is obtained by the action of ammonia on phosphorus tribromide or tri-iodide at −70° (Hugot, Compt. rend. 141, 1235). It is an unstable yellow solid which readily decomposes at 0°, forming phosphorimide, $P_2(NH)_3$, a brown solid which decomposes on heating into ammonia, nitrogen, and phosphorus (v. also Stock, Ber. 1903, 36, 1120).

Phosphamide (*phosphodiamide*) $PO(NH)NH_2$ is a white powder obtained by the action of water on the product of the action of ammonia on phosphorus pentachloride:

$$PCl_5 + 4NH_3 = (NH_2)_2PCl_3 + 2NH_4Cl$$

and

$$(NH_2)_2PCl_3 + H_2O = PO(NH)NH_2 + 3HCl.$$

Phosphoryl triamide (*phosphotriamide*) $PO(NH_2)_3$ is a white amorphous powder obtained by the action of dry ammonia on phosphorus oxychloride (Schiff, Zeitsch. offentl. Chem. 5, 600).

Phosphorus diamide $POH(NH_2)_2$ is obtained by the action of ammonia on a solution of phosphorus oxide in ether or benzene. It is a white powder which dissolves in water with incandescence and is violently decomposed by dilute hydrochloric acid, forming phosphine, phosphorus and phosphorous acids, ammonium chloride and phosphorus (Thorpe and Tutton, Chem. Soc. Trans. 1891, 1627).

Phosphamidic acid or **amidophosphoric acid** $PO·NH_2(OH)_2$ is formed by the action of dry ammonia on phosphorus pentoxide (Stlitz, Ber. 1894, 27, 1237); or the potassium salt of the acid is obtained by the action of potassium hydroxide on the corresponding phenyl ester, the free acid being formed by the decomposition of the lead or silver salt by sulphuretted hydrogen and precipitating it from the citrate with alcohol (Stokes, Amer. Chem. J. 1893, 15, 198; 16, 154). In freezing mixtures microscopic crystals having a sweet taste and forming both acid and acid salts.

Diamidophosphoric acid $PO·NH_2(OH)$ is a crystalline compound obtained in the same way as the foregoing acid (Stokes, *ibid.* 1893). It forms the silver salts $NH_2·PO·Ag$ and $NH_4·PO·Ag$.

A number of similar phosphorus acids have also been prepared (Stokes, Amer. Chem. J. 1894, 16, 123; 1896, 18, 629).

Phosphoryl nitride (*phosphomonamide*) PON is obtained when phosphamide is heated to redness out of contact with air. Several phosphamic acids, and amides containing chlorine, are also known (v. Gladstone, Chem. Soc. Trans. 1864, 225; 1865, 1; 1866, 1 and 290; Salzmann, Ber. 1874, 7, 494; Winter, J. Amer. Chem. Soc. 1904, 26, 1484; Stokes, Amer. Chem. J. 19, 782).

Compounds of phosphorus and sulphur.

Several liquid and solid sulphides, all of which are very inflammable and more fusible than either of the constituent elements, are known. The liquids SP_4 and SP_2 are not compounds but only solutions of sulphur in phosphorus (Boulouch, Compt. rend. 1902, 135, 165; Stock and Bezhold, Ber. 1908, 41, 657; Stock, *ibid.* 1909, 42, 2062). The solid sulphides, P_4S_3, P_4S_6, and P_2S_5 are obtained by carefully heating sulphur with amorphous phosphorus. The composition P_4S_6 (Dupré) or P_4S_{12} (Berzelius, Gmelin's Handb. 2, 218) has been assigned to a body obtained in rhombic sulphur-like crystals by solution of sulphur in sulphur diphosphide. According to Ramme (Ber. 1879, 12, 940, 1350), the crystals are merely sulphur containing phosphorus (*cf.* Boulouch, Compt. rend. 1906, 143, 41).

Phosphorus pentasulphide P_2S_5, which is employed in the preparation of organic sulphur compounds, is produced by gently heating a mixture of excess of powdered roll sulphur and amorphous phosphorus. A small portion of the mixture is first heated in a stream of carbon dioxide until reaction sets in. The source of heat is then removed and the rest of the mixture is added in small quantities. After cooling, the mass is extracted with boiling carbon disulphide (Stock and Scharfenberg, Ber. 1906, 41, 558). The product forms a greyish-yellow crystalline mass, which may be obtained in transparent crystals by sublimation. According to Stock and Thiel (Ber. 1905, 38, 2719), the pentasulphide exists in at least two modifications. The ordinary compound melts at 274°-276° (Meyer, *ibid.* 1879, 12, 610), and boils at 519° at 734 mm. pressure (Goldschmidt, *ibid.* 1882, 15, 304). The other modification melts at about 255°, is more soluble in carbon disulphide and can be obtained by the distillation of the ordinary sulphide is cooled and rapidly cooling the product (Stock and Scharfenberg, l.c.).

Phosphorus pentasulphide dissolves in liquid ammonia forming ammonia thioimidophosphate compounds from which imidothiophosphoric acid has been obtained (Stock, Ber. 1906, 39, 1967).

Phosphorus sesquisulphide P_4S_3 forms rhombic prisms m.p. 166°, b.p. 408°. It is easily inflammable and is slowly decomposed by boiling water forming sulphuretted hydrogen, phosphine, and phosphorous acid (Harris, Chem. Soc. Proc. 1892, 181; *ibid.* 1893, 231; Mai and Scheeder, Ber. 1903, 36, 570. The commercial product sometimes contains free phosphorus, the presence of which can be detected by passing a current of hydrogen over the sulphide which, if phosphorus is present, takes fire.

In carbon disulphide solution, phosphorus

former. Should the bath be too acid after making, a little sodium carbonate may be added. The following are convenient quantities for the preparation of larger amounts of bath solution—

	For negatives	For positives and ferrotypes
Silver nitrate (recrystallised)	6 oz.	6 oz.
Distilled water	80 oz.	80 oz.
Nitric acid	10 min.	12 min.

Saturate with an iodide as before described, and filter.

Development of the latent image. The chemistry of the action of the wet plate process has been already indicated. It is only necessary now to give formulæ best adapted to the development of the image. Those relate particularly to the acid development collodion process.

The following table gives the quantities necessary for some useful iron developers for wet plates :—

	a	b	c	d
Ferrous sulphate	75 grs.	180 grs.	100 grs.	—
Ammonio-ferrous sulphate	—	—	—	125 grs.
Copper sulphate	—	—	50 grs.	—
Barium nitrate [1]	—	120 grs.	—	—
Acetic acid	120 min.	120 min.	100 min.	125 min.
Alcohol	120 „	—	100 „	125 „
Nitric acid	3 „	10 min.	—	—
Water	5 oz.	5 oz.	5 oz.	5 oz.

In the wet-plate process the development may be carried out by pouring a sufficient quantity of the fluid over the plate, or the plate may be immersed in a dish as in the case of dry plates. When sufficient detail has made its appearance, the excess of developer is washed off by a stream of water.

Intensification of wet plates. When the density of the negative is not sufficient for printing purposes, it may be strengthened by pouring over the plate a sufficient quantity of either of the following solutions :

	a	b
Pyrogallol	10 grs.	—
Citric acid	20 grs.	50 grs.
Ferrous sulphate	—	25 grs.
Water	5 oz.	5 oz.

After the plate has been thoroughly moistened with the solution, the latter is poured back into the developing-glass and a few drops of a 10-grain solution of silver nitrate added to it. On re-flooding the plate with the mixture, the image will gradually gain in density. Other substances may be employed as intensifiers, some of which will be mentioned in connection with dry plates, but for a full description of the various formulæ text-books on photography must be consulted.

Fixing. To remove the unacted-upon silver salt, sodium thiosulphate or potassium cyanide may be employed ; the solution being contained in a flat dish, or in an upright bath provided with a dipper. The following quantities are those generally employed for plates—

	a
Sodium thiosulphate	4 oz.
Water	20 oz.

[1] The insoluble barium sulphate formed is filtered off ; *b* is suitable for positives.

	b
Potassium cyanide.	120 grs.
Water	5 oz.

a is preferred for negatives, *b* for positives. Great care is required in the employment of the latter salt on account of its very poisonous character.

Varnishes.—For the protection of films they should be covered with a coating of varnish as clear and as hard as possible, to prevent damage during the operation of printing. These varnishes are resins dissolved in such solvents as alcohol, benzene, or chloroform. The composition of some of these is kept secret, but the quantities given in the next column yield good material for ordinary work.

a and *c* are suitable for negatives, *c* being very hard and durable. *b* may be rubbed off for retouching the negative, and should not be used when great permanency is required. For further details with regard to photographic varnishes *v.* VARNISH.

	a	b	c	d
Shellac	150 gr.	—	—	—
Sandarac	150 „	384 gr.	—	430 gr.
Mastic	60 „	—	—	—
White hard varnish	—	—	3 oz.	—
Camphor	3 gr.	—	—	—
Oil of lavender	—	5 dr.	—	1 dr.
Chloroform	—	2 „	—	—
Oil of turpentine	½ dr.	—	—	3 dr.
Venice turpentine	½ dr.	—	—	—
Alcohol	5 oz.	5 oz.	5 oz.	5 oz.

DRY PLATE PROCESSES.

Collodion emulsion. Next to the wet plate process come the more modern or emulsion processes, which may conveniently be divided into those containing collodion, and those containing gelatin as the thickening medium in the emulsion. Gelatin emulsions are now the most important ; but, the others being useful for certain purposes, the production of a collodion emulsion is briefly described before proceeding to those in which gelatin is employed.

The plates having been prepared and edged, if necessary, as previously described, may be coated with an emulsion prepared in the following manner. The plain collodion may be made by dissolving 200 grains of ordinary pyroxyline in 5 ounces of alcohol (sp.gr. 0·820) mixed with 10 ounces of ether (sp.gr. 0·730). To make. say, 1 pint of emulsion from this, after the final treatment of emulsification, drying, washing, and re-emulsifying has been gone through, we may take 7½ ounces, or the half of the collodion prepared. 200 grains of zinc bromide are next weighed out in two portions of 100 grains each, one of these portions being dissolved in the smallest quantity of alcohol ; 4 or 5 drops of nitric acid are added to the solution, and then poured into the collodion. The second 100 grains are dissolved in a boiling tube in alcohol, 10 drops of nitric acid added, and kept ready for use. Next 330 grains of silver nitrate are weighed out and dissolved in about 5 to 6 drs. of water, and 10 drops of nitric acid added to the solution. To

mixture .to cool, the emulsion is found precipitated at the bottom of the vessel. The precipitated emulsion can then be washed in a stream of water, and transferred to a covered pot until required for coating the plates.

The numbers just given will be found convenient for a beginner making an emulsion for the first time. and yield one of moderate rapidity. The following table gives a selected series of emulsions suitable for different purposes. Nos. I. and II. are of different degrees of rapidity, the first yielding a material suitable for landscapes, when no great rapidity is required : the second deals with an emulsion of greater sensitiveness.

Table of Various Gelatino-Bromide Emulsions.

—	I.	II.	III.	IV.	V.	VI.
A (Silver nitrate	200 grains	200 grains	400 grains	200 grains	330 grains	462 grains
Distilled water	3 ounces	3 ounces	7 ounces	3 ounces	3 ounces	10 ounces
Ammonia (·880)	—	—	{ sufficient to dissolve ppt. }	—	—	{ sufficient to dissolve ppt. }
B (Ammonium iodide	—	—	24 grains	—	—	—
Ammonium bromide	—	—	280 grains	120 grains	200 grains	—
Potassium bromide	160 grains	165 grains	—	—	—	370 grains
Gelatin (Nelson's No. 1)	40 grains	30 grains	80 grains	30 grains	218 grains	615 grains
Hydrochloric acid (1 p.c. sol.)	200 mins.	—	—	—	—	—
Distilled water	2½ ounces	2½ ounces	5¼ ounces	4 ounces	3 ounces	10 ounces
C (Potassium iodide	12 grains	6 grains	—	—	—	—
Distilled water	¼ ounce	½ ounce	—	—	—	—
D (French gelatin	—	—	—	—	218 grains	—
Hard gelatin	300 grains	250 grains	—	200 grains	—	—
Water	4 ounces	3 ounces	—	—	3 ounces	—
E (Methylated spirit	—	—	2¼ ounces	—	—	—
Salicylic acid	—	—	25 grains	—	—	—

For more detailed information regarding the manufacture, ripening. &c., of gelatin emulsions the various text-books on photography must be consulted.

For coating ordinary-sized plates with emulsion on a small scale the following method may be employed. The plate must be laid on a very accurately-levelled stand or tripod. A quantity of emulsion sufficient to cover nearly half the plate is poured on the middle of it : a glass rod about 2 ins. longer than the width of the plate is then grasped between the fingers and thumbs of both hands, dipped across the plate, into the middle of the pool of emulsion, and steadily moved first to one end and then to the other of the plate. By a motion of the finger and thumb the rod can be raised a slight distance from the plate, so as to allow the emulsion to coat smoothly, and, by resting the tips of the finger and thumb upon the levelled slab, a guiding motion may be given to the rod. In the large manufactories many mechanical arrangements are employed to facilitate rapid coating of the plates.

When the emulsion is thoroughly set on the plates, they are removed from the level slab to a suitable rack to undergo a thorough drying process. This is most conveniently done in a specially-constructed drying-box with a current of air artificially heated from the outside passing through it. The artificial heating of the air is unnecessary if the air-passages are sufficiently large and properly arranged.

The plates will take from 12 to 48 hours to dry, according to circumstances, and may then be packed until required for use.

Ortho - chromatic photography. On comparing the curves indicating the intensities of the visual and the photographed spectrum, it will be at once observed that very little relation exists between them, the visual intensity being greatest about the points D and C, and the photographic intensity about the point G in the spectrum, gradually diminishing to the points marked F and E (Fig. 6).

The object of ortho-chromatic photography is by the use of certain dyes introduced into the sensitive material to bring the visual and the photographic intensity as much into harmony as possible. This unison may be partially brought about by the introduction into the photographic film of substances such as eosin, erythrosin, rose of Bengal, cyanin, &c.

The most important work in the direction of ortho-chromatic photography has been carried out by Becquerel, Eder, and Vogel on the continent : Cary Lea in America, and by Abney, Waterhouse, and C. H. Bothamley in this country. The dyes are now generally incorporated with the sensitive film, but may also be used in the form of screens placed in close juxtaposition to the plate.

The amount of dye employed must be small, as the effect is destroyed by large quantities. When mixed with the emulsion it is generally found best to employ about 15–30 min. for every 500 c.c. of emulsion ; but when the sensitive plate is dipped in the dye a solution of 1 part of dye in 20,000 of water is sufficient.

Orthochromatic plates may be divided into (1) those sensitive to the green and yellow rays, (2) to orange and red rays, and (3) to the entire

spectrum (panchromatic). There are many sensitive substances employed, but the following table shows some of those most commonly used :—

		a	b	c
I.	Erythrosin	10 grs.	—	—
	Cyanine blue (ethyl cyanine or pinacyanol)	—	1 gr.	—
	Auracine	—	—	1 gr.
	Alcohol	4 oz.	8 oz.	—
	Water	—	—	10 oz.
II.	Ammonia (0·880)	1 dr.	—	1 dr.
	Water	24 oz.	—	—

(a) is suitable for the green-yellow region, and if the plate be coated with the sensitiser by dipping, it should be used within a few days. (b) is for the red region. These plates from their sensitiveness must be prepared practically in the dark. (c) is for green and blue-green rays. The auracine is dissolved in boiling water, filtered, and the ammonia added to the cooled solution. This solution reduces the speed of the plate.

For panchromatic plates the two following solutions may be used : (d) alcoholic solution of pinachrome (1 : 1000); ammonia (0·880), 5 min.; water, 1 oz.; (e) alcoholic solution of homocol (1 : 1000); ammonia, 10 min.; water, 1 oz.

Special care must be taken in preparing these plates, which should be done somewhat quickly, and in the dark.

Many other sensitisers may be used, of which the following are instances. For blue-green and green, acridine orange without ammonia. For green and yellow (but not red) erythrosin as above. Green, yellow and red, orthochrome, pinaverdol, pinachrome or homocol. Extreme visible red, pinacyanol. Infra-red, dicyanine.

The following curves, taken from Bothamley's papers on this subject, show the increased sensitiveness produced by some of these dyes in the portion of the spectrum lying between A and E :—

I	Visual intensity.
II	Gelatino-bromide undyed.
III	Ammoniated eosin.
IV	Ammoniacal erythrosin.
V	Ammoniacal rose Bengal.
IV	Ammoniacal cyanine.

Fig. 6.

The following diagrams indicate the increased sensitiveness of (a) an isochromatic plate showing partial sensitiveness; and (b) a panchromatic plate with the sensitiveness extending into the red rays.

Spectrum of Isochromatic Plate

Fig. 7(a).

Spectrum of Panchromatic Plate

Fig. 7(b).

The chief use for plates so sensitised will be found in the copying of pictures, flowers, or distinct patterns of different colours, where as much harmony as possible is required between the visual and photographic effect but they will also prove useful in harmonising contrasts sometimes found in portraiture.

For detailed information on ortho-chromatic photography special papers relating to the subject should be consulted.

DEVELOPMENT OF DRY PLATES.

The development of dry plates produced either by collodion or gelatin emulsion is carried out either by iron-salts—such as ferrous oxalate or ferrous citro-oxalate—or by what is termed 'alkaline development,' in which pyrogallol, hydroquinone, amidol, or some other organic-reducing agent, associated with the bromides of potassium or ammonium as retarders, and with ammonia, or the carbonates of potassium or sodium, as accelerators of the reducing action.

Development with ferrous oxalate. This method is simple for ordinary dry plates, and may be employed for negatives on paper, or enlargements on gelatino-bromide paper, but it does not permit correction of inaccurate exposure to such an extent as the pyro-developer. The ferrous oxalate developer may be prepared by adding 1 volume of a saturated ferrous sulphate solution to 4 volumes of a saturated solution of potassium oxalate. Such solutions are obtained by dissolving 4 oz. of neutral potassium oxalate and 6 oz. ferrous sulphate separately, each in 10 oz. of water. A solution of potassium bromide, containing 20 grs. bromide to the oz. of water, should also be made : of this, about 4 drops should be taken for every 2½ oz. of developer. The ferrous oxalate developer is specially applicable in the development of transparencies or positives made with gelatino-chloride or collodio-chloriode emulsions. It is, however, generally found better for this last-named emulsion to employ a ferrous-citro-oxalate, or ferrous citrate developer, with which, by varying the amount of the accelerator, graduated tones may be given to the transparency. The quantities given in the following table may be regarded as good standard quantities to be selected from :—

In many cases the organic developer and the alkaline accelerator may be mixed together in one solution. The following may be taken as typical developers of this class :—

		a	b	c	d	e	f	g
Organic Developers.	Eikinogen	120 gr.	—	—	—	—	—	—
	Glycin	—	160 gr.	—	—	—	—	—
	Hydroquinone	—	—	50 gr.	65 gr.	—	25 gr.	—
	Formalin	—	—	—	1½ dr. fl.	—	—	—
	Metol	—	—	—	—	75 gr.	18 gr.	—
	p.-Aminophenol	—	—	—	—	—	—	480 gr.
Accelerator.	Sodium carbonate	240 gr.	—	720 gr.	—	840 gr.	360 gr.	—
	„ sulphite	480 gr.	240 gr.	360 gr.	1440 gr.	600 gr.	480 gr.	—
	Potassium carbonate	—	800 gr.	—	—	—	—	—
	„ bromide	—	—	—	—	8 gr.	—	—
	„ metabisulphite	—	—	—	—	—	—	1440 gr.
	Water	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.

As a rule these developers should be diluted with an equal quantity of water immediately before developing. With developer (e) for portraits take equal parts of stock solution and water ; for landscapes 1 part of stock to 2 of water.

The glycin developer (b) is a slow developer, but particularly suitable for 'stand development.'

In commencing the development of a plate it is better to begin with a less quantity of the accelerator than the full amount stated, and gradually add the remainder as development advances.

The darkening of the film when the alkaline pyrogallol developer is used must not be allowed to go on so long as with the ferrous oxalate developer. In the former case the image is of a slightly yellow tinge, and consequently of a more non-actinic nature than that formed by the oxalate. As has been already stated it is not absolutely necessary that three separate solutions be kept, but this course is better so as to facilitate the retardation of development on over-exposure, or its acceleration on under-exposure. If proper exposure has been given the image will appear in about one minute, and gradually gain in strength. When all the details are visible, and the development apparently stops, a few more drops of the accelerator may be poured into the developing cup, the developer mixed with it. and again flowed over the plate. This fresh addition of the alkali rapidly produces increase of density. When the development is deemed complete, wash thoroughly in a gentle stream of water from the rose-tap and place in the fixing-bath. unless it be deemed necessary to soak the plate in an alum solution to prevent frilling.

For the special development of dry plates for transparencies, or slides to be used in the lantern, the developers given in the following table will be found useful, and will give different tones to the transparencies :—

Pyro and Ammonia Developer for Warm Tones.

I.	Pyrogallol	1 oz.
	Sodium sulphite	4 oz.
	Citric acid	½ oz.
	Water	16 oz.
II.	Ammonium bromide	1 oz.
	Liquor ammonia (0·880)	5½ dr.
	Water up to	16 oz.

For use mix 1 part of No. I. with 3 parts of No. II. and dilute to double the quantity with water. The mixed developer may be used for several plates.

Developers for Black Tones.

	a	b
Hydroquinone	60 grs.	—
Amidol	—	80 grs.
Sodium carbonate	4 oz.	—
„ sulphite	2 oz.	2 oz.
Potassium carbonate	2 oz.	—
„ bromide	40 grs.	½ oz.
Water	20 oz.	12 oz.

These developers may be used for several plates, and will keep good for some time. In almost all cases it will be found best to use the developer which is generally described on the box of the special plate used.

Many operators now prefer a fixed time development during which the plate if properly exposed need not be examined. This is carried out in a closed box or tank, of which many forms are on the market. Tables are also given by which the time necessary for different developers may be calculated.

Intensification and reduction of dry-plate negatives. If proper exposure be given to the plate the process of development by the ferrous salt or by pyrogallol will always yield sufficient printing density. Both under- or over-exposure, however, will yield an image far too thin to give a vigorous and brilliant print. This deficiency may be remedied to a certain extent by the process of intensification ; but it must be understood that the results, when such a process has to be employed, are never so brilliant as with a properly-exposed and properly-developed negative.

Several methods are in general use for the intensification of dry plates, one of the most usual being that in which the action is carried out by a mercury salt and ammonia. In dry plate work the process of intensification is almost invariably carried out after fixing. For this purpose it is necessary that the last traces of sodium thiosulphate should be removed from

the negative by thorough washing. Should it be necessary to take still further precautions for the removal of the last traces of thiosulphate, the negative should be soaked in a saturated solution of alum containing 3 grains of citric acid to the ounce of solution, or in a solution of hydrogen peroxide containing 1 drachm of 'hydrogen peroxide solution' to 5 oz. of water. The plate may be soaked in these from 10 to 30 minutes, and again washed before intensification.

To intensify, first thoroughly soak the plate in water to soften the film, then place in the following solution, preferably in a black vulcanite dish :—

I.

Mercuric chloride . .	200 grs.
Ammonium chloride . .	200 grs.
Water	10 oz.

The plate rapidly undergoes a process of bleaching, and when the film is bleached throughout it is removed from the solution and thoroughly washed under the tap. The washing in this case must be most thorough. After this washing the plate is flooded with a solution of ammonia :

II.

Ammonia, 0·880 . . .	1 part
Water	10 parts

In this solution the plate rapidly assumes density, becoming changed first to a rich non-actinic brown, and finally to black, according to the length of time it has been left in the mercury bath.

The plate may also be intensified by one or other of the following solutions :—

	a	b	c	d
Sodium sulphite	1 part	—	—	—
Ferrous oxalate	—	ordinary developer	—	—
Hydroquinone	—	—	ordinary developer	—
Uranium nitrate	—	—	—	1 part
Potassium ferri-cyanide	—	—	—	1 ,,
Acetic acid (glacial)	—	—	—	10 parts
Water . .	6 parts	—	—	100 ,,

(a), (b), and (c) are to be used after the negative has been bleached by the mercuric chloride solution ; (d) is an intensifier by itself.

In all cases the plates should be well washed between the application of solutions I. and II. and after intensification ; they may also be placed in the fixing bath again for a minute or two with advantage, and then finally washed.

Reducing negatives. Should the negative after development and fixing appear too dense for printing purposes, one of the following courses of treatment will cause its reduction :—

(1) Soak the plate carefully in sodium thiosulphate solution (2 oz. to 1 pint) to which has been added potassium ferricyanide sufficient to give it a yellow colour. The reduction in this case takes place with considerable rapidity, and a stream of water or a washing dish should be handy for immersion of the negative to check too rapid reduction.

(2) Immerse the moist negative in one of the following solutions :—

	a	b	c	d
Potassium ferric oxalate	150 grs.	—	—	—
Sodium sulphite .	125 ,,	—	—	—
Oxalic acid .	45 ,,	—	—	—
Sodium thiosulphate	1½ oz.	—	—	—
Ammonium persulphate	—	15 grs.	—	—
Potassium permanganate (10 p.c. solution)	—	—	1 dr.fl.	—
Potassium dichromate	—	—	—	100 grs.
Sulphuric acid (10 p.c. solution) .	—	—	5 dr.fl.	7 dr.fl.
Water . . .	7 oz.	1 oz.	10 oz.	20 oz.

Fixing the negative. This operation is practically the same for dry plates as has already been described for wet plates, except that sodium thiosulphate is always employed and not potassium cyanide. The usual strength of the solution is 4 oz. of thiosulphate to 1 pint of water, but this may be varied according to the experience of the operator.

Transparencies. When a positive picture is required for enlargement, or for showing on a screen to an audience, it is found more convenient to employ an emulsion of gelatin and silver chloride, alone or a mixture of the silver chloride and bromide. The following quantities may be taken as giving emulsions suitable for this purpose :—

		I.	II.
A	Gelatin (Nelson No. 1) .	300 grs.	80 grs.
	Ammonium bromide .	—	210 grs.
	Ammonium chloride .	100 grs.	—
	Sodium chloride .	—	50 grs.
	Hydrochloric acid .	—	5 mm.
	Water . .	10 oz.	10 oz.
B	Silver nitrate .	240 grs.	400 grs.
C	Hard emulsion gelatin .	—	400 grs.

In No. 1 allow the gelatin to soften and swell in the water ; then place all three vessels in a water-bath at a temperature of 120°F. (49°C.). When the gelatin is melted add the silver solution to it, and then stir in the ammonium chloride solution. Allow the emulsion to ripen at that temperature for an hour, and pour out into a dish for setting. The details of washing, coating, and drying the plates, are the same as for the bromide emulsions already described.

As the film left by gelatino-chloride plates after development and fixing is extremely clear in the high lights, it is necessary for these plates to employ glass perfectly free from flaws or air bubbles.

Gelatino-chloride plates are less sensitive to light than the bromide plates, so that for contact transparencies from well-defined negatives, the exposures are proportionately longer.

These plates may be developed by ferrous oxalate, or by the mixture of ferrous oxalate and citrate previously mentioned, or by the hydroquinone developer.

Gelatino-bromide plates also yield good transparencies, but if they are used for this purpose a fairly strong pyro-developer should be taken and the development carried out quickly.

Transparencies are now commonly made by sensitive carbon tissue (v. Carbon processes).

the middle of the convex side of the sheet lowered on to the solution in the dish. After 2 to 3 minutes raise, and again lower, to avoid air bubbles. Float on the solution for 2 to 5 minutes, then hang up to dry.

To sensitise the paper. A silver solution, stronger than that used for sensitising the plate must generally be employed. The following give varying strengths for different circumstances :—

Silver nitrate	a 50 grs.	b 80 grs.	c 30 grs.
Water (distilled)	1 oz.	1 oz.	1 oz.

a may be used for ordinary cases, *b* where the negative is weak, and *c* where the lights and shades on the negative show great contrast. The strength of the bath becomes gradually lowered, and must be restored from time to time. Only strong negatives should be printed in direct sunlight; all other cases should be exposed only to diffused daylight or covered with tissue paper or ground glass during printing.

Toning. To obviate the red colour of the printed image, it is immersed in a neutral solution of gold containing certain metallic salts. The following are some selected toning baths :—

——	a	b	c	d	e
Gold chloride	1 gr.	1 gr.	1 gr.	1 gr.	1 gr.
Sodium acetate	30 grs.	—	—	—	—
„ phosphate	—	20 grs.	—	—	—
„ bicarbonate	—	—	30 grs.	—	—
„ biborate (borax)	—	—	—	20 grs.	—
„ tungstate	—	—	—	—	20 grs.
Water	10 ozs.	10 ozs.	10 ozs.	10 ozs.	10 ozs.

a is a good bath for ordinary use, giving purple-brown tones, but should be made up 12 hours before use ; *b*, *c*, and *d* can be used shortly after making, and give purple tones, but do not keep well ; *e* gives fine purple-brown tones, and keeps fairly well in the dark. These solutions may also be made up in strong solutions by dissolving the tube of 15 grs. of gold in 15 oz. of water, and adding the proper quantity of alkaline salt. To make the bath for immediate use mix 1 part of the stock solution with 10 oz. of water.

The chemical reactions taking place in the process of toning do not appear to be complex in their nature, the tone being produced by a fine film of gold, reduced from a neutral solution of gold chloride ($AuCl_3$), or of the double salt ($NaAuCl_4$, $2H_2O$), upon the film containing the reduced products from the silver chloride and albuminate. To obtain the best results the gold solution must be neutral or very slightly alkaline.

Fixing the print. This is done by immersing the print, after toning, in a solution of sodium thiosulphate, 4 oz. in 20 oz. of water. This strength is suitable for prints from strong negatives, but where the print is weak the fixing bath may be reduced to 3 or 2 oz. of thiosulphate to the pint of water. Before fixing, the prints should be immersed in water containing a small quantity of sodium carbonate for 10 minutes, and then placed face downwards in the fixing bath. Their brilliancy will at first diminish, but

will to a certain extent be restored when they are finally fixed and dried. The prints should remain in the fixing bath from 10 to 15 minutes, being gently moved about to prevent them sticking together. The prints must be washed after fixing for at least 24 hours in different changes of water, or for 6 in running water.

In silver printing the toning bath should be neutral or slightly alkaline, and not below 60°F. The prints must be printed rather darker than finally required, and toned to a chestnut brown, or purple.

Printing with gelatino-chloride emulsions. More rapid printing may be effected by the use of a chloride emulsion on paper, as the copy may either be printed to the full extent in a bright light, or the image if imperfectly printed may be fully developed as in the case of a plate or film transparency. The following gelatino-chloride emulsions will be found useful for such papers.

Gelatin	340 grs.	{Nelson's No.1 {Colgnet's	87 grs. 87 „
Ammonium chloride	11 „	. . .	18 „
Alum	15 „		
Rochelle salt	15 „	. . .	50 „
Water	6½ oz.		
Silver nitrate	115 „	. . .	75 „
Citric acid	62 „		
Alcohol	.	. . .	4 drs.
Water	1 oz.	. . .	5 oz.

Rapid printing with gelatino-bromide paper. Paper coated with gelatino-bromide emulsion is also largely used for printing by artificial light and for purposes of enlarging. The materials and details for coating are much the same as described for the manufacture of plates or films on celluloid.

The exposures may be made by artificial light. After exposure the prints may under general conditions be developed, if necessary, intensified, or reduced, and finally fixed by the solutions already mentioned for bromide plates or films. If desired they may be toned by the gold or platinum solutions already given under *Toning* formulae, and other colours may be given to them by the use of certain salts. Thus dark brown to red tones may be obtained by using copper salts ; green tones by mixed vanadium and iron salts ; and blue tones by iron salts. For the development and subsequent treatment it is best to use the special formulae generally issued by the makers with the different varieties of papers. Should a combined toning and fixing bath be not used, the prints, after toning, must be fixed in the usual way.

The tone of these prints is distinctly neutral and somewhat like platinum prints. The print may be obtained dull by allowing it to dry on blotting paper after final washing, with the sensitised side upwards, or it may be obtained with a glossy appearance by being 'squeegeed,' face downwards, on a glass or ferrotype plate and allowed to dry in that position. When dry, it may be stripped from off the plate.

The printing, like that with albumenised paper, should be carried slightly further than the shade finally required, as the prints diminish in intensity during toning and fixing with certain baths.

ferric oxalate and sodium oxalate; small quantities of potassium chlorate and mercuric chloride being also introduced under certain circumstances. This method differs from the other two in that the paper contains the sensitive salt and developer upon it during exposure, the printing of the image being carried to its full extent. Under the influence of light and the moisture in the air, reduction of the platinum salt takes place in the printing-frame. The printing must be continued until the picture has the appearance finally required. In moist weather the printing will go on without difficulty; in very dry weather the increase of density apparently stops after a certain intensity has been reached; it will continue, however, to print, if the back of the paper be breathed upon or very gently steamed.

Fixing the prints. This is best done by placing the prints in 1 vol. hydrochloric acid and 60–80 vols. water till the high lights appear perfectly white. They should then be washed in several changes of water. The tone given by platinum prints is especially applicable for copying buildings and machinery, but also yields most beautiful effects in portraiture when the proper lighting of the original negative has been attended to.

PRINTING WITH IRON SALTS.

Several processes have been brought forward in which the salts of iron may be employed instead of those of silver and platinum, thus rendering the cost of copying large plans or drawings much less expensive.

The reduction of the ferric salts by light was first utilised by Sir John Herschel, who employed ferric ammonium citrate as his sensitive material, developing the image with a solution of potassium ferricyanide, and the different methods now employed are more or less modifications of his original process.

By mixing the ferric salt and potassium ferricyanide together before coating the paper, the print may after exposure be developed by merely washing in water until the washings are colourless. For such a paper the following mixture will be found useful :—

I. { Potassium ferricyanide . 200 grs.
   { Distilled water . . 5 oz.

II. { Ferric ammonium citrate . 600 grs.
    { Distilled water . . 5 oz.

Dissolve the salts separately, then mix, keep the solution in the dark, and filter before use. The paper, after coating and drying, must be kept for a few days before use. When thoroughly exposed the print should show a bronze colour in the shadows and is developed by soaking in one or two changes of water. The colour of the prints may be improved by soaking after development in a solution of 2½ p.c. alum and 3 p.c. oxalic acid.

A method for obtaining positive prints from positives may be carried out by sensitising the paper with the following solution :—

I. { Gum arabic . 4 oz.
   { Water . . . 20 „

II. { Ferric ammonium
    { citrate . . 10 „
    { Water . . . 20 „

III. { Ferric chloride . 10 „
     { Water . . . 20 „

Mix 8 vols. of II. then 5 vols. of III. to 20 vols. of I. in small portions with constant stirring.

The paper, having been coated, dried, and exposed in the ordinary manner, may be developed by floating it on a solution of 1 oz. potassium ferrocyanide in 10 oz. of water. After development immerse in a 1 p.c. cleansing solution of hydrochloric acid or 1 : 25 sulphuric acid (sp.gr. 1·98), wash thoroughly, and dry. These methods are extremely useful for copying large line drawings or diagrams, but may also be used for ordinary landscape and portrait prints.

In the Kallitype process the paper may be sensitised by a mixture containing 75 grs. of ferric oxalate with 30 grs. silver nitrate to 1 oz. of water. The ferric oxalate is dissolved in the hot water with a grain or two of oxalic acid to assist solution. After filtering the silver is added and the solution kept in the dark.

The following may be taken as developers for this paper :—

	a	b	c
Borax	2 oz.	¼ oz.	—
Rochelle salt	1¼ oz.	2 oz.	1 oz.
Potassium dichromate (1 p.c. solution)	15–18 drs.	15–18 drs.	8–10 drs.
Water	20 oz.	20 oz.	20 oz.

(*a*) yields black, (*b*) purple, and (*c*) sepia tones. The prints are fixed in a solution of sodium thiosulphate in 20 oz. of water to which 120 min. of ammonia (0·880) has been added.

Numerous papers for printing from negatives by silver, platinum, or other metallic salts can now be used. The formulæ and details necessary for working the individual processes are best obtained from the directions issued by the various makers.

DIAZOTYPE.

Under this heading may be classed two processes for printing in colours which may be shortly described in an article on photography. The one devised in Germany is termed *Feer-type* (from the inventor); the other is the *Primuline process*, introduced in England by Messrs. Green, Cross, & Bevan.

In the *Feer-type* the material is sensitised with a mixture of a diazo compound with a phenol or amine in molecular proportions, dried in the dark and exposed behind a negative. The azo colouring matter is produced in quantities proportional to the amount of light passing through the negative. After printing, the material is dipped in very dilute hydrochloric acid, and finally washed with water. The following table gives instances of some of the mixtures employed :—

	I.	II.	III.
	Parts	Parts	Parts
Sodium toluenediazo-sulphonate	25	—	—
Sodium ditolyl-tetrazo-sulphonate	—	25	25
β-naphthol	25	—	—
m-Phenylenediamine	—	20	—
Resorcinol	—	—	12
Sodium hydroxide	8	—	16
Water	1000	1000	1000

points a, a, a, the rays intersect each other, giving no movement at these points, and, consequently, no light effect, whereas at the points b, b, b, or internodal points as they are called, where no interference exists, the action of light will cause a deposition of silver. This deposition taking place at a separation of half a wave length of the incident, light will only reflect light of the colour, the wave length of which is double the distance of these internodal points.

Originally Lippmann employed an albumen process for his sensitive plates, colour-sensitised with erythrosin, quinoline red, cyanine, and malachite green; but more recently formulæ for gelatin emulsion plates have been put forward by Valenta, Lumière, and by Lippmann himself. The following numbers give two forms of the emulsions that have been proposed :—

		I.	II.
A.	Gelatin	10 grs.	5 grs.
	Silver nitrate	6 grs.	3 grs.
	Water	300 c.c.	225 c.c.
B.	Gelatin	20 grs.	5 grs.
	Potassium bromide	5 grs.	2·1 grs.
	Water	300 c.c.	225 c.c.

For colour sensitising cyanine and erythrosin solutions (1 : 500) have been used. For the sensitiser 2 parts of the cyanine solution is mixed with 1 part of the erythrosin solution, and 1 to 2 parts of this mixture added to 100 parts of the emulsion. Increased sensitiveness may be given to these plates by bathing them shortly before exposure in a mixture of 5 grams of silver nitrate dissolved in 1000 c.c. of alcohol, to which 5 c.c. of acetic acid have been added.

Ives' process. This process, devised by Ives in America and by Ducos du Hauron in France, depends on the principle put forward by Clerk Maxwell, that the object to be reproduced, if photographed through three separate coloured screens, will give corresponding negatives representing in light and shade the gradation to which the different light effects coming from the object will excite a single primary colour sensation in the eye. Three negatives of the object are obtained, one taken behind an orange screen, a second behind a green, and a third behind a blue screen. Three positives are then taken from these negatives, and are illuminated one by red, the second by green, and the third by blue violet light. These being superimposed on a screen, the combined image of the original object will be seen reproduced in its natural colours.

For the simultaneous production of the negatives and for the projection on the screen, special cameras have been devised, and for viewing the transparencies Ives introduced the apparatus known under the name of the ' Kromoscope.'

The same effect may be obtained on one glass plate in the following way. Three separate negatives are taken, paying due attention to the exposures necessary for the different coloured filters. These are developed in the usual way, fixed and washed. To obtain positives from these negatives, an ordinary transparency is first taken from the negative obtained through the red screen, washed and dried. It is then bleached by immersion for about a minute in a solution of potassium ferricyanide, washed with water, and placed for a minute and a half in the red staining solution. The stained film is then transferred to a solution of sodium thiosulphate, which at first causes a brown precipitate. This is at once thrown off and fresh thiosulphate flowed over the plate, when the image will gradually assume a greenish-blue colour. The plate is now washed, dried, varnished with a celluloid enamel, and again dried.

The pink and yellow images may then be printed at the same time on one strip of a sensitised dichromated gelatin film, the celluloid side of the film, not the dichromated side, being in contact with the film side of the negative, so that the print is made through the celluloid support. The film is then developed in the usual manner by hot water at a temperature of 95°–100°F., fixed by sodium thiosulphate, and thoroughly washed with cold water. The two prints are now cut separate and stained by the pink and the yellow dyes. The staining should be carried out in white porcelain dishes, and should be done slowly.

When the stained transfers have been rinsed and dried they are ready to be superimposed in correct position over the blue transparency first described. The pink film is first accurately adjusted film to film over the blue, and then the yellow, stained side downwards, over the pink. The films may be fixed in accurate register with binding slips, but a better result is obtained if the separate films are secured in optical contact by Canada balsam. When thrown on the screen the original picture is reproduced.

Dyes for tri-colour staining. The following are some of the substances which may be used. For blue : thio blue A or soluble Prussian blue, slightly acidified with sulphuric acid. For pink : a mixture of eosin and rhodamin pink. For yellow : best brilliant yellow or aniline yellow. For Ives' plates. For blue : methylene blue, 16 grs. ; cold water, 4 oz. For pink : magenta red, 16 grs. ; hot water, 4 oz. ; acetic acid, 10 mins. For yellow, ammonium picrate, a saturated solution. In each case the transfer, after staining, should be rinsed in water slightly acidified with acetic acid.

The nature of these dyes is very varied, and special works must be consulted with regard to quantities and methods of preparation.

Light filters for colour work. These may be made with either a collodion or a gelatin medium coated on glass or used in cells. For yellow light filters : tetrazine, rapid filter yellow K ; aurantia, and naphthol yellow may be used. For orange filter a mixture of aurantia or rose Bengal with tetrazine is employed.

Filters for three-colour work. For these a 6 p.c. stock gelatino solution is the medium. For the violet filter (yellow printing negative), stock dye solution, crystal violet, 31 grs. ; warm water, 6 oz., 76 mm. ; glacial acetic acid 3 mm. Add 20 parts dye solution to 100 parts gelatin solution. A second blue dye is rapid filter blue, 15½ grs. ; water, 6 oz., 160 mm. ; ammonia, 10 mm. Filter, then take dye solution 20 parts ; gelatin, 100 parts. For green filter (red printing negative). Rapid filter green I., 62 grains ; water 3½ oz. Take of dye solution 20 parts to 100 of gelatin solution. A green for

varying size, which are capable of producing the illusion of shading. The 'grain' can be varied to suit the subject; and the finer the detail to be rendered, the finer the 'grain' should be. The ink image is eventually transferred to stone (v. also *Collotype*). From the finished stone, transfers can be taken which can be utilised in the production of a series of new stones, which after careful modification by hand can be employed in the production of pictures in colours by chromo lithography.

Photozincography and photoalagraphy are processes in which zinc and aluminium are used in place of the lithographic stone as the printing surface, and the methods employed are similar to those described.

Collotype. A collotype print is a picture in varnish ink obtained from the surface of chromated gelatin which is supported upon a rigid body, generally glass. Such a surface is produced by exposing the dichromated gelatin-coated glass under a negative and afterwards removing the unaltered chromium salt by washing in cold water, when the film is dried spontaneously. If the film be afterwards moistened with an aqueous solution of glycerol and ammonia, such solution will be absorbed, and the gelatin will swell slightly. If the excess of such 'damping' solution be removed and a charged roller be passed over the surface, the ink from the roller will be taken by the different parts of the film proportionally to the amount of light action which has taken place during the exposure under the negative, and this ink may be readily transferred to paper by simple pressure. By this process it is therefore possible to render automatically by purely chemico-physical means the gradations of light and shade in the negative in such a form as to be utilisable in the printing press. It is interesting to compare this process with Woodburytype, where the translation is mechanical, and with the half-tone block process, where it is produced by optical means.

Provided that a suitable negative be made, any subject can be rendered in collotype. The plates may be printed in the press, where the manipulations are wholly by hand, or in the machine, where the damping, inking, and printing are mechanical. The rate of printing of the best class of collotype is slow. The process is valuable for the reason that it is capable of yielding pictures the gradations of which are faithful to the negative and, as compared with the half-tone block process, without the disturbing effect of the regular dot formation. The variety of printing paper that can be used is considerable, and because of this fact the process has additional value.

For the preparation of the printing surface a sheet of plate glass, ¼ to ⅜ inch in thickness is finely ground upon its surface and is then flowed over with a solution of an alkaline silicate and white of egg. After evaporation of the water, the plate is heated to about 60°. It is then cooled and washed in cold water and afterwards allowed to dry. This process is termed 'substratuming,' and its purpose is to cause a deposit of silica upon the glass. This deposit, in addition to the roughness of the glass, causes the subsequent film of gelatin to adhere strongly. This device is necessary

owing to the mechanical strain upon the film caused by the operations of rolling and printing.

The sensitive film is produced by coating the plate with a solution of gelatin and alkali dichromate in water. The gelatin used must be of high grade and of medium 'hardness' and free from fatty matter. The prepared glass is warmed and levelled, and the requisite quantity of the solution is poured upon the surface and spread, preferably by the clean finger. Drying must take place by evaporation at an elevated temperature—there is no intermediate setting to form a 'gel.' Upon correct conduct of this drying the success of the plate maker largely depends. To this end, the plate rests upon levelling screws in a drying oven, which is a box—generally constructed of wood—large in volume, and kept at the suitable temperature by means of a steam or hot-water radiator. Gas or oil heating may be used, provided that care is taken to prevent the products of combustion entering the chamber containing the plates. The construction of the oven must be such that there is no internal vibration and that there are no 'draughts.' Failing these conditions the film will dry with an uneven surface—a fatal defect. The top of the box must be covered with a fabric which will permit the passage of the water vapour from the plates out of the oven.

The oven temperature, varied between 40°-60°, influences the character of the film. When the film of gelatin is dry the oven is allowed to cool, and afterwards the plates are removed and are kept in the dark. The films will remain in good condition for 1-2 days, depending upon the atmospheric surroundings. If, however, storage takes place in an artificially dried atmosphere, as in a storage box containing a tray full of calcium chloride, the plates may be kept 5-6 days. Deterioration is due to spontaneous insolubilisation of the film. For collotypes, laterally inverted negatives are required. In practice, the plates are printed (exposed), in the case of small pictures, from glass-plate negatives. More perfect contact between the surfaces is obtained by printing from flexible film negatives prepared for the purpose, which are laid upon the plate glass bed of the printing frame. By means of thin tin foil such negatives are masked at the margins to show only the amount of subject required. Exposure takes place in the ordinary way, but the frames have usually no backs, so that the under side of the film may be examined in order to observe the progress of printing. The film darkens in proportion to the duration of exposure. Usually, the printer determines the correct amount required by judgment. When the plate has been exposed sufficiently, it is removed, and is then quickly and evenly immersed in water or it may be flooded. Washing continues until the free dichromate is removed, when the film will be practically without colour. It is then dried. Examination of the plate before drying, at this stage, shows that the image is in slight relief and that it is reticulated. A certain amount of 'grain' is required to ensure successful printing at the press, but such 'grain' should not be obvious to the unaided eye. The following conditions influence the character of the 'grain':

always leads to a flattening of the contrast. Although 'fine etching' of half-tone plates is to a considerable extent employed to alter the appearance of the pictures as presented by the proofs from the plates—of illustrations, indeed, which are not satisfactory to those who wish to use them even before they are reproduced—the process would, to some extent, be necessary in the case of good originals because of the flattening effect of the screen. When drawings are to be reproduced by these methods and have to be made for the purpose, allowance is generally made for the reduced contrast by forcing the effect in the drawing, hence 'drawings,' for process, which are generally made in monochrome body colour although useful for the purpose intended, are of little value afterwards for obvious æsthetic reasons.

Any drawing in line, even those made without any regard to reproduction processes, where beautiful effect is the only consideration, may be successfully translated, but only by the expenditure of extra time and skill. Disregarding pictorial drawings, much technically unsatisfactory 'copy' is dealt with in the ordinary way. When drawings in line are made, however, with a view to reproduction in the commercial way, they are generally prepared in black line upon white card.

By far the larger amount of half-tone illustrations to catalogues (especially those showing machinery) and publications of a similar commercial character are prepared from photographs which have been 'worked up' by the draughtsman, who changes the appearance of the original by modifying portions, by suppression, or by addition, and this to such an extent that the photograph is completely changed. Such 'working up' is carried out by means of the 'air brush,' a pen-like tool by means of which a fine stream of air can be caused to project a spray of liquid pigment upon a surface, the effect producible being entirely under control, and moreover—which is the important feature—with that smoothness and continuity which is a characteristic of the shading in a photograph, so that the added work is in harmony with the print. It is largely owing to this that the photo-engraver has almost entirely replaced the wood engraver in the preparation of the illustrations for the best classes of catalogue.

C. W. G.

PHOTOLITHOGRAPHY r. Photography.

PHOTOPHONE r. Selenium.

PHOTOSANTONIC ACID r. Santonica.

PHTHALEÏN DYES r. Triphenylmethane colouring matters.

PHTHALIC ACID. The three dicarboxylic acids of benzene are known as the phthalic acids. Of these the only one of technical importance is *ortho*phthalic acid $C_6H_4\begin{smallmatrix}COOH\ (1)\\ COOH\ (2)\end{smallmatrix}$ and this is the compound which is always understood when the name *phthalic acid* is used without further qualification, the meta-compound being distinguished as *iso*phthalic acid and the para- as *tere*phthalic acid.

ortho-Phthalic acid was first obtained by Laurent in 1836 by the oxidation of naphthalene (Annalen, 19, 38), and the same coal-tar product

has always served as the chief source of this valuable acid—

Naphthalene.

$$+ 4O_2 =$$

o-phthalic acid.

$$+ \begin{smallmatrix}COOH\\ COOH\end{smallmatrix}$$

Similarly other di-substitution derivatives of benzene containing carbon chains or groups in the ortho- position yield phthalic acid on oxidation, e.g. in addition to naphthalene cited above, tetrachloronaphthalene, alizarin, purpurin, o-toluic acid, have been employed, along with such oxidising agents as dilute nitric acid, alkaline permanganate, chromic acid, sulphuric acid (Marignac and others, Annalen, 42, 215; 66, 197; 75, 12, 25; 130, 334; 144, 71; 148, 60; Ber. 6, 945; 7, 1057; 12, 579; 18, 1499; Zeitsch. Chem. [ii.], 4, 551,705; Compt. rend. 56, 82; Frdl. 1897-1900, 664).

A variety of other methods are known, e.g. the action of potassium ferrocyanide and sulphuric acid on salicylic acid, or of formic and sulphuric acids on salicylic acid; interaction of resorcinol and sodium bicarbonate; by the reaction between benzyl chloride, carbon tetrachloride and nitric acid; or by acting upon benzene or benzoic acid with pyrolusite and concentrated sulphuric acid in the cold.

Häussermann (J. 1877, 763, 1158) describes a method suitable for laboratory preparation, from 2 parts of potassium chlorate in 10 parts of commercial hydrochloric acid and 1 part of naphthalene, which mixture is gently heated, chlorination first taking place and then oxidation. The product is washed with water and with light petroleum, and afterwards 10 parts of nitric acid (sp.gr. 1·45) is gradually added and the mixture boiled. When all dissolves, the nitric acid is evaporated and the residue distilled; phthalic anhydride passes over, which may be further purified by sublimation, and reconverted into phthalic acid by boiling with caustic soda and acidifying the cold solution with mineral acid. The precipitated phthalic acid is best purified by recrystallising from boiling water.

Physical properties. It exists in trimetric plates; whole crystals melt at 213°; when powdered, at 205°, passing into the anhydride. Sp.gr. 1·585-1·593; 100 parts of water at 14° dissolve 0·54 parts of acid, and at 99° 18 parts of acid (Graebe, Annalen, 1887, 238, 321). Phthalic acid is readily soluble in alcohol, sparingly so in ether and insoluble in chloroform (hence separation from benzoic acid); it is slightly volatile in steam. The acid shows an absorption band in the spectrum, but the anhydride does not. It is said to form a eutectic mixture with its anhydride (de Stadt, Zeitsch. physikal. Chem. 41, 353. For measurements of conductivities reference should be made

to the work of Jones (Amer. Chem. J. 42, 520; 43, 187; 44, 159); Sidgwick (Chem. Soc. Trans. 1910, 97, 1677); Godlewski (Chem. Zentr. 1904, [ii.] 1275).

Chemical properties. Phthalic acid forms a characteristic, sparingly soluble barium salt (Carius, Annalen, 1868, 148, 60; Hermann, Annalen, 1874, 171, 78), and also forms salts with most metallic oxides, including bismuth, yttrium (J. pr. Chem. [ii.] 74, 142; Bull. Soc. Chim. [iii.] 31, 135; J. Russ. Phys. Chem. Soo. 42, 586). Calcium phthalate on heating gives benzophenone, benzene, carbon dioxide, small quantities of other hydrocarbons and anthraquinone. The acid itself, when heated with excess of lime, yields benzene and calcium carbonate, calcium benzoate being formed as an intermediate product. The acid is very stable towards sulphuric acid, merely passing into its internal anhydride with loss of water; more strongly heated it loses a little carbon dioxide and is sulphonated. With sulphuric acid it is also said to form a definite additive compound, $C_8H_6O_4+H_2SO_4$ (Hoogewerf and van Dorp, D. R. P. 21352). Michaelis has prepared a phthalo-arsenic acid $(COOH)_2 \cdot C_6H_3 \cdot AsO(OH)_2$ (Annalen, 320, 271).

The *constitution* of the acid has been solved by Nölting (Ber. 1885, 18, 2687) who by oxidising the three xylenes with permanganate obtained excellent yields of the phthalic acids. As meta-xylene forms three isomeric nitro-xylenes, xylidenes and xylenols, ortho- two, and para- only one each of these derivatives, therefore *iso*-phthalic acid has positions 1, 3, ordinary phthalic 1, 2, and tere-phthalic 1, 4, for the carboxyl groups.

Phthalic anhydride is formed (1) by distillation of the acid, (2) by warming the acid with acetyl chloride (Laurent, Marignac), (3) by interaction of lead nitrate and phthalyl chloride (Lachowicz, Ber. 1884, 17, 1283), (4) by heating phthalonic acid—itself an oxidation product of naphthalene—to 200°, (5) dissolving the acid in phenol, anisole, or veratrole, containing P_2O_5 (Gazz. chim. ital. 30, ii. 361), (6) shaking a solution of sodium phthalate with two molecules of acetic anhydride (Gazz. chim, ital. 26, ii. 482). All these methods are represented ultimately by the equation—

$$\begin{array}{ccc} \begin{array}{c}COOH\\ \\ COOH\end{array} & = & \begin{array}{c}CO\\ \\ CO\end{array}O + H_2O \end{array}$$

Phthalic anhydride.

o-Phthalic acid is the only one of the three isomerides which gives in this way an *internal* anhydride. A novel method of preparation is given by Denham (Chem. Soc. Trans. 1909, 95, 1235) from the interaction of sulphur monochloride on the sodium salt—

$$C_6H_4(COONa)_2 \rightarrow C_6H_4(COOS)_2$$
$$\rightarrow C_6H_4{<}^{CO}_{CO}{>}O$$

The anhydride exists as long, tough needles, m.p. 128°, b.p. 284°; it is very sparingly soluble in cold, more readily so in hot, water, being gradually reconverted into phthalic acid; in alcohol and ether it is readily soluble, and dissolves in alkalis forming phthalates. With dry ammonia it gives phthalimide (*see* below); with alcoholic ammonia phthalamic acid,

$C_6H_4(CONH_2)COOH$, m.p. 149°; and with aqueous ammonia it yields ammonium phthalamate $C_6H_4(CONH_2)COONH_4$, which on heating is transformed into phthalimide (*see* later).

Fusion of phthalic anhydride with lime produces benzene and diphenyl (Annalen, 1879, 196, 48); with zinc dust it gives biphthalyl, $C_{16}H_8O_4$, and with zinc dust and methyl iodide yields dimethyl phthalide $C_6H_4{<}^{CMe_2}_{CO}{>}O$.

In contact with alkaline hydrogen peroxide it reacts with formation of monoperphthalic acid, $COOH \cdot C_6H_4 \cdot CO \cdot O \cdot OH$ and the external anhydride of this. Three molecules of phthalic anhydride combine with 2 molecules of $SbCl_5$ to form a crystalline compound.

The usual method for the detection of small quantities of phthalic anhydride is that of fusion with about twice the weight of resorcinol in presence of a drop of concentrated sulphuric acid. In this way fluorescein is produced (*v. infra*), and the reddish-brown product, when dissolved in dilute caustic soda and poured into a large volume of water, yields a magnificent green fluorescent solution. This reaction is shown by all the ortho-dicarboxylic acids of the benzene series, although with the formation of a variety of coloured solutions, but it is not shown by the meta- or para-dicarboxylic acids. Succinic anhydride shows an analogous reaction.

A method for the quantitative estimation of phthalic anhydride in presence of a number of impurities is described by Boswell (J. Amer. Chem. Soc. 1907, 29, 230). It consists in the careful sublimation of the anhydride and subsequent titration with standardised caustic soda.

TECHNICAL MANUFACTURE.

Owing to the extensive use of phthalic anhydride in the manufacture of synthetic indigo (*q.v.*) and the pyronine and triphenylmethane class of dye-stuffs, a cheap technical process for its preparation in large quantities was essential, and this has been achieved in the various patents of the Badische Anilin u. Soda Fabrik (*cf.* D. R. P. March 31st, 1896, 91202; Eng. Pat. 18221, August 17th. 1896; Frdl. 1894-1897, 164), which are based upon the observation that naphthalene is readily oxidised by concentrated sulphuric acid containing mercuric sulphate, its oxide, or the metal itself, which acts as a catalyst, and that the sulphur dioxide formed by the reduction of the mineral acid is reconverted into sulphuric acid by absorption of oxygen from the air, the whole process being practically continuous.

In the English patent the quantities given are as follows :—

100 kilograms naphthalene
1500   ,,   sulphuric acid (100 p.c. H_2SO_4)
50   ,,   mercuric sulphate.

In place of naphthalene, β-naphthol, naphthionic acid, or phenanthrene may be used. The mercury sulphate remains behind as residue in the retort and is used over and over again.

It should be borne in mind that a too vigorous oxidation will destroy the phthalic acid as soon as formed, and therefore the preparation should be conducted within well-defined limits of temperature—about 270°-300°.

and nitrophenols by the action of alkalis under pressure and in a dilution medium such as common salt.

Esters of phthalic acid with most of the known alcohols have been prepared in the usual way. The dimethyl ester distils at 280°/734 mm.; diethyl ester at 295°; diphenyl ester melts at 73°; benzyl acid ester has m.p. 106°-107°, affording a good characterisation of benzyl alcohol; cyclohexanol acid ester, m.p. 99°, neutral ester m.p. 66°. Various esters of phthalic acid are used as solvents for resins, e.g. copal resin, which need not be melted to be dissolved (Hesse, D. R. P. 227667).

Pickard has accomplished the resolution of various complex alcohols into their optically active components by making the acid-ester by simple fusion with phthalic anhydride and combining this with active bases (Chem. Soc. Trans. 1907, 91, 1974).

Ethyl phthalate reacts with ethyl acetate and sodium to form ethyl diketohydrindene carboxylate; and with ethyl propionate and sodium, yielding methyl diketohydrindene—

$$C_6H_4\underset{CO}{\overset{CO}{<}}>CH \cdot CH_3$$

If ethyl succinate be substituted for ethyl propionate, ethyl dihydronaphthraquinone dicarboxylate is formed.

Derivatives and Condensation Products of Phthalic Anhydride.

The extraordinary reactivity of the anhydride accounts for the great number of important derivatives which have been prepared. First among these should be mentioned *phthalyl chloride* $C_6H_4\underset{CO}{\overset{CCl_2}{<}}>O$, obtained by the action of phosphorus pentachloride. It is a liquid of b.p. 275°/726 mm., solidifying at 0°C. From this, by the action of ethyl alcohol, is obtained the ether, $C_6H_4\underset{CO}{\overset{C(OEt)_2}{<}}>O$, while it also condenses with ketones or with ethyl sodio-acetate (Fischer and Koch, Ber. 16, 651; Bülow and Koch, Ber. 1904, 37, 577 : 1905, 38, 474). Reduction of phthalyl chloride with zinc and hydrochloric acid produces the important derivative *phthalide* $C_6H_4\underset{CO}{\overset{CH_2}{<}}>O$, m.p. 73° (v. LACTONES), and with acetic acid and sodium amalgam the phthalyl alcohol, $C_6H_4\underset{CH_2OH}{\overset{CH_2OH}{<}}$.

Grignard's reagents act on phthalic anhydride, forming the dialkyl and diaryl *phthalides*, of which a large variety have been prepared :—

$$C_6H_4\underset{CO}{\overset{CO}{<}}>O + RMgBr$$

$$\rightarrow C_6H_4\underset{CR_2(OH)}{\overset{COOH}{<}} \rightarrow C_6H_4\underset{CR_2}{\overset{CO \cdot}{<}}>O$$

(cf. Bauer, Ber. 1904, 37, 735; 1905, 38, 240;

Arch. Pharm. 247, 220). Pickles and Weizmann (Chem. Soc. Proc. 1904, 20, 201) have prepared *mono*-aryl hydroxyphthalides by this means, which give by the action of water keto acids; anthraquinone has thus been prepared by the following series of reactions :—

$$C_6H_4\underset{CO}{\overset{CO}{<}}>O + MgBrC_6H_5$$

$$\rightarrow C_6H_4\underset{CO}{\overset{C(C_6H_5)(OH)}{<}}>O$$

$$\rightarrow C_6H_4\underset{COOH}{\overset{CO \cdot C_6H_5}{<}} \rightarrow C_6H_4\underset{CO}{\overset{CO}{<}}>C_6H_4$$

Simonis and Arand (Ber. 1909, 42, 3721) have succeeded in obtaining acyl benzoic acids by the interaction of Grignard reagents and phthalic acid itself, in addition to the dialkyl phthalides just described, e.g. using excess of magnesium ethyl bromide he isolated o-carboxy-phenyl ethyl ketone, m.p. 97°, $C_6H_4\underset{COOH}{\overset{COC_2H_5}{<}}$.

Phthalic anhydride condenses with the cresols or their methyl ethers in presence of boric acid or aluminium chloride (cf. phthalein reaction with phenol) :

$$C_6H_4\underset{CO}{\overset{CO}{<}}>O + C_6H_4(CH_3)OCH_3$$

$$\rightarrow C_6H_4\underset{COOH}{\overset{CO \cdot C_6H_3(CH_3)OCH_3}{<}}$$

$$\rightarrow C_6H_4\underset{CO}{\overset{CO}{<}}>C_6H_3(CH_3)OCH_3.$$

Sulphuric acid effects the closing of the ring in the condensation product, giving oxy-methyl anthraquinones and their methyl derivatives (v. METHYL ANTHRACENE; cf. Bentley, Gardner, and Weizmann, Chem. Soc. Trans. 1907, 91, 1626; Lambrecht, Ber. 1909, 42, 3591). The simplest case of the above condensation was worked out by Friedel and Crafts, who condensed phthalic anhydride and benzene in presence of aluminium chloride, with the ultimate formation of anthraquinone :—

$$C_6H_4\underset{CO}{\overset{CO}{<}}>O + C_6H_6 \rightarrow C_6H_4\underset{COOH}{\overset{CO \cdot C_6H_5}{<}}$$

$$\rightarrow C_6H_4\underset{CO}{\overset{CO}{<}}>C_6H_4 + H_2O$$

(V. ANTHRAQUINONE, also Friedel and Crafts, Ann. Chim. Phys. [vi.] 14, 446; Heller, D. R. P. 193961.)

Phthalic anhydride condenses with phenols in presence of a dehydrating agent like zinc chloride or sulphuric acid, yielding a class of colouring matters known as the phthaleins. which are fully dealt with in the article on TRIPHENYLMETHANE COLOURING MATTERS. The simplest member of the series is phenolphthalein, prepared by condensing phthalic anhydride with 2 molecules of pheno (Baeyer, Ber. 1874, 7, 968)—

$$C_6H_4\underset{CO}{\overset{CO}{<}}>O + 2C_6H_5OH$$

$$= C_6H_4\underset{CO}{\overset{C(C_6H_4OH)_2}{<}}>O + H_2O.$$

Phenolphthalein.

When resorcinol is substituted for phenol in this condensation, the product is the beautiful green fluorescein acid. the sodium salt of which is known in commerce as the dyestuff uranine—

Fluoresceïn.

Eosin is another well-known member of this series of colouring matters, and is a bromo derivative of fluoresceïn.

Catechol condenses with phthalic anhydride in presence of concentrated sulphuric acid with formation of hystazarin and alizarin :

Hystazarin.   **Alizarin.**

An interesting condensation is that carried out by Marchese (Gaz. chim. ital. **37**, ii. 303). Phthalic anhydride was caused to react with 2 molecules of sodium hydrindene carboxylic ester in presence of acetic anhydride, with the formation of the complex, anhydrophthalo-bisdiketo-hydr¹ndene, m.p. about 325°—

In many reactions phthalic anhydride shows a similarity to aldehydes. It is attacked by nitromethane in ether solution at 10°, and on adding methyl alcohol and sodium ethoxide, two products are isolated (Gabriel, Ber. 1903, **36**, 570)—

$$C_6H_4{<}^{COOMe}_{COOH} \text{ and } C_6H_4{<}^{C(OH) \cdot CH_2 \cdot NO_2}_{CO}{>}O$$

Again, phthalic anhydride condenses with 1 molecule of α-picolene just as does acetaldehyde or benzaldehyde, yielding in this case γ-pyro-phthalone—

$$C_6H_4{<}^{C(: CH \cdot C_5H_4N)}_{CO}{>}O$$

this being known as the ' phthalone reaction ' (Düring, Ber. 1905, **38**, 161). The same reaction occurs with quinaldine (Eibner, Ber. 1904, **37**, 3605) with the lutidines, in some cases using zinc chloride (Scholze, Ber. 1905, **38**, 2806; Langer, ibid. 3704). with α-methyl indol (Fischer, Annalen, 1887, **242**. 381), and with cotarnine (Knoll and Co., D. R. P. 175079).

With *amines* and *amino acids*, phthalic anhydride gives an important series of compounds of the type, $C_6H_4{<}^{CO \cdot NHR}_{COOH}$ or the

anhydride of this (cf. Tingle, J. Amer. Chem. Soc. 1910, **32**, 113 and 1319). An example is that of glycine and phthalic anhydride, which give phthalyl glycine

$$C_6H_4{<}^{CO}_{CO}{>}N \cdot CH_2 \cdot COOH,$$

the ester of which Gabriel and Colman (Ber. 1902, **35**, 2534) have converted into an *iso*-quinoline derivative on heating; hydrolysis of this leads to the compound (I.), which with nitric acid yields the interesting substance, phthalonimide (II.), m.p. 224°, a compound obtained also from carbindigo—

Andreasch has prepared in this way the phthalyl-alanine (m.p. 164°) (Monatsh. **25**, 774; cf. also Fischer, Ber. 1907, **40**, 489 ; and Annalen. 1888, **248**, 152—for taurine). With benzidine the condensation is effected in aqueous solution, giving the compound—

$$C_6H_4{<}^{CO-NH \cdot C_6H_4}_{CO-NH \cdot C_6H_4}$$

(Koller, Ber. 1904, **37**, 2880).

Sodium benzamide or sodium acetamide give the acyl phthalaminic acids (Titherley, Chem. Soc. Trans. 1906, 89, 708), which pass into the acyl phthalimides on dehydration with acetyl chloride—

$$C_6H_4{<}^{COOH}_{CO \cdot NH \cdot CO \cdot R} \rightarrow C_6H_4{<}^{CO}_{CO}{>}N \cdot CO \cdot R$$

Some applications of the above reactions to the preparation of dyestuffs are given :—

p-chlor-quinaldine condensed with phthalic anhydride and sulphonation of the quinophtha-lone so formed—

leads to a valuable yellow quinoline dyestuff (Bayer and Co., D. R. P. 204255; Eng. Pat. 1908, 28266: Frdl. 1908-1910. 280).

α-aminoanthraquinone in nitrobenzene condenses with phthalic anhydride in presence of phosphorus pentachloride yielding an orange-yellow dye (D. R. P. 216980; Eng. Pat. 27098, 1901; Frdl. 1908-1910, 753). Dyestuffs of the *acridine series* may be obtained by heating phthalic anhydride with phenylene or toluylene diamines in presence of the hydrochlorides of these bases, with or without a condensation agent such as zinc chloride (D. R. P. 141356; Eng. Pat. 11711, 1902 ; Frdl. 1902, 1904. 316).

Phthalyl chloride condenses with remarkable ease with substances possessing labile hydrogen atoms, which combine with the chlorine atoms causing the evolution of hydrogen chloride, e.g. malonic ester, acetoacetic ester, cyanacetic ester, &c.

Bülow and his collaborators (Ber. 1904. **37**, 4379 ; 1906, 39, 2275) have condensed

it with acetyl acetone, and obtained the products—

$$C_6H_4 \left\langle \begin{array}{c} CO \\ \vert \\ C:C(CO\cdot CH_3)_2 \end{array} \right\rangle O \quad \text{and} \quad C_6H_4 \left\langle \begin{array}{c} CO \\ \vert \\ C:CH\cdot CO\cdot CH_3 \end{array} \right\rangle O,$$

the second of which readily passes into 6-acetyl diketo-hydrindene—

$$C_6H_4 \left\langle \begin{array}{c} CO \\ \vert \\ CO \end{array} \right\rangle CH\cdot CO\cdot CH_3$$

(cf. also Eibner, Ber. 1906, 39, 2202).

THE HYDROPHTHALIC ACIDS.

The classical work associated with the name of von Baeyer on the reduction of the phthalic acids has done much to extend our knowledge of valency, and especially of the constitution of the benzene ring. His researches (Annalen, 1873, 166, 346; 1890, 258, 214; 1892, 269, 164) enunciate the general rule, that entrance of hydrogen atoms into the molecule undergoing reduction, always takes place by attachment first to the α-carbon atoms, i.e. those which are adjacent to carboxyl groups. For example, adopting the special nomenclature for the hydro-benzenes, namely—

then the reduction of ortho-phthalic acid with sodium amalgam in weak acetic acid solution, gave rise to the trans-$\Delta^{3,5}$-dihydrophthalic acid

which melts at 210°. This is also prepared by electrolysis of phthalic acid in hot 15 p.c. aqueous sulphuric acid (Mettler, Ber. 1906, 39, 2941). The cis-form is only obtained by acting on this with acetic anhydride for 7 minutes, when the cis-anhydride, m.p. 100°, is formed, which on boiling with water yields the cis-acid, m.p. 175°; prolonged boiling converts the cis- into trans-form. The above $\Delta^{3,5}$ acid is what is known as a βγ doubly unsaturated acid, the double linkings being both attached to βγ carbon atoms with reference to the carboxyl groups. This type of acid readily undergoes inversion by digesting with alkalis such as caustic soda, due to the shifting of the double bonds to the αβ position in each case, so that the compound

$\Delta^{2,6}$-dihydrophthalic acid

is obtained. This acid is exclusively formed when the reduction of phthalic acid with sodium amalgam is carried out in alkaline solution. It melts at 215°, and its anhydride, formed by

the action of acetyl chloride, melts at 84°. Benzoic acid may be obtained from this $\Delta^{2,6}$-acid on oxidation. It is not affected by boiling with aqueous caustic soda, but very concentrated alcoholic potash produces the

$\Delta^{2,4}$-Dihydrophthalic Acid

which melts at 180°, and which is also obtained indirectly from the dihydrobromide of $\Delta^{2,6}$ dihydrophthalic acid and methyl alcoholic potash. When this $\Delta^{2,4}$-acid is boiled for 6 minutes with acetic anhydride, the anhydride of a new acid,

$\Delta^{1,4}$-Dihydrophthalic Acid

is formed, and on decomposing this with boiling water the above acid is obtained, m.p. 153°. Boiling caustic soda converts it into the $\Delta^{2,4}$ and $\Delta^{2,6}$ isomerides. It may be oxidised back again into phthalic acid. The anhydride of the acid melts at 133°.

Abati and Bernardinis (Chem. Zentr. 1905, i. 1318) have isolated the two remaining dihydrophthalic acids by a careful scheme for separating the initial reduction products obtained as described by Baeyer. These are the—

$\Delta^{1,3}$-Dihydrophthalic Acid

the anhydride of which melts at 59°–60°, and also the

$\Delta^{2,5}$-Dihydrophthalic Acid,

which is obtained by heating the $\Delta^{1,3}$-acid to 230° in a closed tube; also by the intermediate shifting of the double linking in the $\Delta^{3,5}$-acid by means of caustic soda. Its anhydride melts at 73° (cf. also Abati, Gaz. chim. ital. 38, i. 152).

The Tetrahydrides are five in number. On reducing a boiling solution of sodium phthalate with sodium amalgam,

Δ^2-Tetrahydrophthalic Acid

is formed, m.p. 215°; the anhydride melts at 79°, and is made by heating the acid. When this acid is heated for a considerable time at its melting-point, the anhydride of

Δ^1-Tetrahydrophthalic Acid

is produced, which on boiling with water gives rise to the above Δ^1-acid, m.p. 120°. The anhydride melts at 74°. This is also prepared

by distilling the tetrahydride of pyromellitic acid. It changes back into the Δ^2-acid with concentrated potash, and permanganate oxidises it to adipic acid

Trans-Δ^4-tetrahydrophthalic Acid

is formed, together with Δ^2-acid, by reducing the $\Delta^{2,6}$ dihydride in boiling water with sodium amalgam, that is—

(*Cf.* Thiele, Annalen, 1899, 306, 125.) This Δ^4-acid melts at 218° ; its *anhydride*, made by the action of acetyl chloride, melts at 140°, and the *methyl ester* melts at 40°. The acid changes on heating into the *cis-form*, which is also obtained by reducing the $\Delta^{2,4}$-acid at 0° with sodium amalgam. This *cis-Δ^4-acid* melts at 174°, and its *anhydride* at 58°.

The remaining isomeride—

Δ^3-*Tetrahydrophthalic Acid*

is described by Abati and Vergari (Gazz. chim. ital. 1909, 39, ii. 142). Its *anhydride* melts at 70°–71°.

Both the di- and tetra-hydrophthalic acids are unstable towards permanganate and with milder oxidising agents may be oxidised back to phthalic acid. They form, as a rule, additive compounds with bromine or hydrobromic acid, and yield on reduction hexahydrophthalic acid (*cf.* also Graebe and Born, Annalen, 1867, 142, 330 ; Astie, Annalen, 258, 187). The physical properties of all these acids have been carefully measured by Abati and his collaborators (Gazz. chim. ital. 39, ii. 142; Chem. Zentr. 1907, i. 886).

Trans-hexahydrophthalic Acid

is prepared by reducing all the lower hydrides or their halogen additive compounds, either with sodium amalgam or zinc dust and acetic acid. It melts at 221°, and is not oxidised by cold permanganate. The *anhydride* melts at 140°, and the *dimethyl ester* at 33°. When slowly heated, the acid yields the anhydride of *cis-hexahydrophthalic acid*, from which the free acid is obtained by boiling with water. The acid melts at 192°, and the *anhydride* at 32°.

NITROGEN DERIVATIVES.

Phthalimide $C_6H_4{<}^{CO}_{CO}{>}NH$ is formed by the action of ammonia gas on molten phthalic anhydride, and is a most important stage in the manufacturing process of synthetic indigo. The method, due to Kuhara, is a quantitative

one. Dry ammonia gas compressed in cylinders is used, and is passed into the phthalic anhydride until it ceases to be absorbed, the process occupying in all about 18 hours. The chief condition is that at the end of the operation, when complete transformation of anhydride into imide has been effected, the mass should remain in the molten state ; the anhydride melts at 128° and the imide at 228°, hence during the progress of the operation the temperature should be maintained 1° above the latter. The molten product is run off and allowed to cool and crystallised in open pans ; 650 kilos. of anhydride yield 635 kilos. of phthalimide.

Phthalimide may also be prepared by heating phthalic anhydride with urea (Dunlap), or with aliphatic nitriles (Matthews, J. Amer. Chem. Soc. 1896, 18, 680; 1898, 20, 654), or with formamide, acetamide, and other amides, acetanilide, and similar compounds. It exists as colourless plates, m.p. 228°, and may be sublimed.

Reactions.—Amyl alcohol and sodium reduce *phthalimide* to *o*-methyl benzylamine (Bamberger, Ber. 1888, 21, 1888). Distilled with lime, it loses water and carbon dioxide, yielding benzonitrile (Reese, Annalen, 1887, 242, 5). With alcoholic potash it forms a potassium derivative,

$$C_6H_4{<}^{CO}_{CO}{>}NK$$
$$\downarrow$$
$$C_6H_4{<}^{CONH_2}_{COOK}$$

which on boiling with water is converted into potassium phthalamate.

From the point of view of indigo its most important reaction is that discovered by Hoogewerff and van Dorp (D. R. P. 55988), with alkaline KOBr at 80°, when it is transformed into *o*-aminobenzoic acid, or anthranilic acid—

Mohr (J. pr. Chem. [ii.] 80, 1 ; D. R. PP. 127138, 139218 ; Frdl. 1902–1904, 118–120) has modified this by using NaOCl, and states that sodium isatoic acid anhydride is probably formed as an intermediate compound, which excess of caustic soda converts into sodium anthranilate—

Phthalimide forms a potassium derivative exactly as does malonic ester, in which also the metallic radicle may be substituted for alkyl by contact with halogen compounds (*see résumé* by Sörensen, Zeitsch. physikal Chem. 44, 448 ; Chem. Zentr. 1905, ii. 401 ; *cf.* also Bull.

Soc. chim. 33, 1042). Gabriel describes an interesting example of this use of potassium phthalimide with dibromopropane—

$$C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle NK + Br\cdot CH_2\cdot CH_2\cdot CH_2 Br$$

$$\rightarrow C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle N[CH_2]_3 Br$$

with
KOH
$$\rightarrow C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle N[CH_2]_3 OH$$

(Ber. 1905, 38, 2389).

Two molecules of phthalimide may also combine with the halogen derivative, giving

$$C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle N\cdot CH_2\cdot CH_2\cdot CH_2\cdot N\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle C_6H_4,$$

and this on hydrolysis with mineral acids yields trimethylene diamine and 2 molecules of phthalic acid, thus providing an excellent general method for the preparation of diamines.

Various mercaptan derivatives of phthalimide have been prepared by Manasse (Ber. 1902, 35, 1307).

The German patent No. 139553 describes the preparation of *phthal-chlorimide* by leading chlorine into an aqueous suspension of phthalimide.

A 40 p.c. solution of formaldehyde gives with phthalimide a methyl phthalimide of m.p. 132° (Breslauer and Pictet, Ber. 1907, 40, 3784). Various Grignard reagents have been tried with success upon phthalimide (cf. Béis, Compt. rend. 138, 987; Sachs and Ludwig, Ber. 1904, 37, 385). With tin and hydrochloric acid it is reduced to phthalimidine $C_6H_4\left\langle \begin{array}{c} CH_2 \\ CO \end{array} \right\rangle NH$ (Graebe, Ber. 1884, 17, 2598; Annalen, 1888, 247291).

Phthalyl hydrazide $C_6H_4\left\langle \begin{array}{c} CO\cdot NH \\ CO\cdot NH \end{array} \right|$ is made from the anhydride and hydrazine (Curtius, J. pr. Chem. [ii.] 51, 376). The phenyl hydrazine derivatives exists in two forms; the first product of the condensation is probably a simple additive compound—

$$C_6H_4\left\langle \begin{array}{c} COOH \\ CONH\cdot NH\cdot C_6H_5, \end{array} \right.$$

which splits off water in two ways, giving—

$$C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle N\cdot NH\cdot C_6H_5 \text{ and } C_6H_4\left\langle \begin{array}{c} CO-NH \\ CO-N\cdot C_6H_5, \end{array} \right.$$

a Phthalyl phenylhydrazine, m.p. 179°.   β form.

(Dunlap, J. Amer. Chem. Soc. 1905, 27, 1091).

Phthalyl semicarbazide melts at 262°.

Phthalylhydroxylamine. Hydroxylamine condenses with phthalic anhydride in aqueous dilute alcoholic solution or in caustic soda, with formation of phthalylhydroxylamine, m.p. 204°–206° in good yields (Basler Chemische Fabrik, D. R. PP. 130680, 130681). Treatment of the hydrochloride of this with sodium carbonate, and subsequent action of caustic

soda, leads to the formation of anthranilic acid—

$$\left\langle \begin{array}{c} CO \\ C:NOH \end{array} \right\rangle O \xrightarrow{Na_2CO_3} \left\langle \begin{array}{c} COOH \\ CO\cdot NHOH \end{array} \right\rangle \rightarrow \left\langle \begin{array}{c} COOH \\ NH_2 \end{array} \right\rangle$$

(D. R. P. 136788; Frdl. 1902-1904, 117).

Phthalanil $C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle N\cdot C_6H_5$, m.p 205°, is formed by heating 1 molecule of sodium phthalate and 2 molecules of aniline hydrochloride in a closed tube for 6 hours at 200° (J. Amer. Chem. Soc. 1903, 25, 612).

Phthalonitrile $C_6H_4\left\langle \begin{array}{c} CN \\ CN \end{array} \right.$ is obtained from 2-aminobenzonitrile by conversion of the NH_2 group into CN (Pinnow and Sämann, Ber. 1896, 29, 630); and from o-cyanobenzaldoxim by dehydration in contact with acetic anhydride (Posner, Ber. 1897, 30, 1698). It forms odourless needles, m.p. 142°, distils without decomposition, and is volatile in steam. It is transformed into phthalic acid on hydrolysis with concentrated hydrochloric acid.

Seminitrile of Phthalic acid $C_6H_4\left\langle \begin{array}{c} CN \\ COOH \end{array} \right.$ (o-cyanobenzoic acid) is prepared from anthranilic acid by the Sandmeyer reaction (Ber. 1885, 18, 1499); by the action of NH_3 upon phthalyl chloride (Hoogewerff and van Dorp, Rec. trav. chim. 11, 91; cf. Kuhara, Amer. Chem. J. 3, 26; Auger, Ann. Chim. Phys. [vi.] 22, 289); and from benzaldehydeoxime-carboxylic acid by contact with acetic anhydride. It exists as needles melting at 180°-190° and changing simultaneously into phthalimide. Heating with water produces acid ammonium phthalate. The *methyl ester* melts at 51°, and the *ethyl ester* at 70°.

SUBSTITUTED PHTHALIC ACIDS.

Many *chloro, bromo, nitro, sulpho* substituted phthalic acids are known, and references to these are frequent in Beilstein's Handbuch der Organischen Chemie, vol. ii. and its supplement; also Frdl. 1887-1890, 93; Villiger, Ber. 1909, 42, 3529. When phthalic anhydride, dissolved in fuming sulphuric acid, is treated with chlorine in presence of a little iodine (Juvalta, D. R. P. 50177), the following reaction occurs :—

$$C_6H_4\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle O + 4Cl + 2SO_3$$

$$= Cl_2\cdot C_6H_2\left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle O + 2 Cl\cdot SO_3H$$

Separation of the products is possible owing to a difference in solubility of the zinc salts, by a recrystallisation of which three isomerides are separated. The chief product is 3 : 6-*dichloro*) *phthalic acid* (I.), smaller quantities of 3 : 4 (II.- and very little of 4 : 5 (III.), being isolated—

$$\begin{array}{ccc}
\text{Cl} & & \\
\left\langle \begin{array}{c} -COOH \\ -COOH \end{array} \right\rangle & \text{Cl}\left\langle \begin{array}{c} -COOH \\ -COOH \end{array} \right\rangle\text{Cl} & \text{Cl}\left\langle \begin{array}{c} -COOH \\ -COOH \end{array} \right\rangle \\
\text{Cl} & \text{Cl} & \\
\text{I.} & \text{II.} & \text{III.}
\end{array}$$

s

The 3 : 6 acid has m.p. 253°–258°; and its anhydride, m.p. 339°.

These acids are more soluble in water and ether than ordinary phthalic acid, and the anhydrides can be distilled (cf. also Graebe, Ber. 1900, 33, 2019).

A fourth isomeride is described by Crossley and Le Sueur (Chem. Soc. Trans. 1906, 81, 1533), viz. the 3 : 5-*dichlorophthalic acid*

(cf. also Claus, Ber. 18, 1370 ; 19, 3175 : J. pr. Chem. [ii.] 43, 253, 582 ; Le Royer, Annalen, 1887, 238, 350).

3 : 6-*dichlorophthalic anhydride*, which is now a commercial product, has been condensed with the three xylenes and the closing of the ring effected, with formation of dichloro-dimethyl-anthraquinones (Harrop, Norris and Weizmann, Chem. Soc. Trans. 1909, 95, 1312)—

Of the four possible *dibromophthalic acids* only the *para* (3 : 6-), m.p. 135°, is at present made, the yield being 30 p.c. ; 100 grams of dibromo-naphthalene is strongly heated for 2 hours with 2 litres of nitric acid (sp.gr. 1·4) ; first a nitrated product is obtained, and then on evaporation of the mother liquors to one-third the volume, white crystals of the 3 : 6-*dibromophthalic acid* appear (Severin, Chem. Zentr. 1907, i. 1119).

Nitro-phthalic acid. Holleman (Chem. Zentr. 1908, ii. 2011) has studied quantitatively the action of concentrated nitric acid on phthalic acid at 30°, and has found that the product contains 49·5 p.c. of the α- and 50·5 p.c. of the β-*nitrophthalic acid*—

Sulpho-phthalic acids. The Badische Anilin und Soda Fabrik, has obtained an English patent (J. Y. Johnson, No. 18221, August 17, 1896) for the preparation of a disulphonic acid. 100 kilos. of naphthalene is dissolved in 300 kilos. of fuming sulphuric acid (23 p.c. SO₃) and mixed with 1200 kilos. concentrated sulphuric acid (95 p.c.). The mass is heated for 10 hours at about 250° ; a certain amount of phthalic acid distils over during the reaction. The product is neutralised with calcium or barium carbonate and worked up in the usual way. The new *disulphonic acid* of phthalic acid may be separated from water in crystalline nodules in the form of its barium salt.

If the temperature is maintained at about 220°, a *monosulphonate* of phthalic acid is obtained.

Hydroxy-phthalic acids. Bentley and Weizmann (Chem. Soc. Trans. 1907, 91, 98) have sulphonated phthalic anhydride with fuming sulphuric acid (73 p.c. SO₃) at 200° and fused the products with caustic soda, obtaining in this way 4-*hydroxy-phthalic acid*, and as by-product *m*-hydroxybenzoic acid—

and

4-*hydroxy-phthalic acid* melts at 204°–205°, its anhydride at 171°–173° ; the *methoxy acid* at 178° and the anhydride of this at 98°.

The same authors, with Miss Rona Robinson (Chem. Soc. Trans. 1907, 91, 104), prepared 1 : 5-*di-methoxy-naphthalene* and oxidised this with permanganate, obtaining 3-*methoxy-phthalic acid*, m.p. 173°, the *anhydride* of which melts at 160°—

Fusion of the methoxy acid with caustic potash gives rise to the 3-*hydroxy-phthalic acid*, m.p. 150°—

Phthalaldehyde $C_6H_4\!\!<\!\!{}^{CHO}_{CHO}$. When *o*-xylene is brominated it yields the tetrabromide

If 400 grams of this bromide are heated with 360 grams of finely powdered crystalline potassium oxalate in an oil-bath for 40 hours, in contact with 2½ litres of water and 2½ litres of 95 p.c. ethyl alcohol, a clear yellow solution results, with evolution of some carbon monoxide and dioxide. After distilling off 2 litres of alcohol, which is used again subsequently, 700 grams of crystalline sodium phosphate are added, and the mass is subjected to distillation in steam, which drives over the phthalic aldehyde. The product is readily soluble in water, and therefore the distillate is extracted several times with acetic ester, which dissolves out the aldehyde, a 90 p.c. yield being obtained in the form of yellow needles, m.p. 56° (Thiele and Günther, Annalen, 1906, 347, 106).

Strong alkali converts phthalaldehyde into phthalide, which appears to be an intramolecular change into a more stable isomeride—

$$C_6H_4\!\!<\!\!{}^{CHO}_{CHO} \rightarrow C_6H_4\!\!<\!\!{}^{CH_2}_{CO}\!\!>\!O$$

It is interesting to compare this with the 'lactone tautomerism' of aldehydo phthalic acid and hydroxy phthalide, which can react in either form—

$$C_6H_4\!\!<\!\!{}^{CHO}_{COOH} \rightarrow C_6H_4\!\!<\!\!{}^{CH\cdot OH}_{CO}\!\!>\!O$$

Phthalaldehyde condenses readily with a large number of substances by virtue of its two —CHO groupings ; e.g. with acetone it

yields β-acetyl hydrindone (Thiele and Falk, Annalen, 1906, 347, 112; 1909, 369, 287)—

$$C_6H_4{<}^{CHO}_{CHO} + CH_3{\cdot}CO{\cdot}CH_3$$

$$= C_6H_4{<}^{CH_2}_{CO}{>}CH{\cdot}CO{\cdot}CH_3 + H_2O$$

Phthalonic acid $C_6H_4{<}^{COOH}_{CO{\cdot}COOH}$, m.p. 144°–145°, is formed at an intermediate stage of the oxidation of naphthalene to phthalic acid, especially when the reagent used is permanganate (Annalen, 1887, 240, 142 ; Daly, J. Phys. Chem. 11, 93). It is also produced by the action of nitric acid on tetrachlor-ketohydrindene (Zinke and Fries, Annalen, 1904, 334, 342). Its *acid methyl ester* melts at 79°–81°, and its neutral *methyl ester* at 66°–68° (cf. Frdl. 1894–1897, 162-163 ; D. R. PP. 79693, 86914 (Tcherniac)).

Phthalonic acid takes part in numerous reactions, principally those involving the keto group : e.g. it condenses with o-phenylene diamin (Gazz. chim. ital. 1904, 34, i. 493), giving the compound—

A warm sodium bisulphite solution of sodium phthalonate gives on evaporation and subsequent treatment with hydrochloric acid, *aldehydo-phthalic acid* (Wegscheider and Bondi, Monatsh. 26, 1039)

$$C_6H_4{<}^{CO{\cdot}COOH}_{COOH} \rightarrow C_6H_4{<}^{CHO}_{COOH} + CO_2$$

The following is the best method of preparing phthalonic acid : 10 grams naphthalene is dissolved in 1 litre of water and 90 grams pure KMnO₄, or its equivalent of the commercial permanganate, is added, and the whole boiled until the solution is completely decolourised. The removal of the excess of naphthalene (2·5 grams) is effected by steam distillation, the oxide of manganese is filtered off, and the filtrate evaporated and then acidified and the product extracted or allowed to crystallise. The yield is 9 grams of phthalonic acid and 1 gram of phthalic acid.

isoPhthalic acid (meta-phthalic acid)

is prepared by the oxidation of m-xylene with permanganate (Nölting, Ber. 1885, 18, 2687) or with chromic acid (Fitting and Velguth, Annalen, 1868, 148, 11 ; 1870, 153, 268) ; or by converting m-xylene into the dibromide by bromination at 125°, treating this with hot alcoholic potash, and oxidising the resulting ether with chromic acid mixture (Kipping, Ber. 1888, 21, 46). It is also obtained by fusing potassium formate with potassium benzoate (Richter, Ber. 1873, 6, 876), or with potassium m brombenzoate (Ador and Meyer, Annalen, 1871, 159, 16), or with benzene disulphonic acid (Barth and Senhofer, Annalen, 1871, 159, 228) ;

and by the action of a hot solution of cuprous potassium cyanide on m-diazobenzoic chloride and saponification of the resulting nitrile (Sandmeyer, Ber. 1885, 18, 1498).

It exists in the form of long slender needles when crystallised from water, which melt at about 300° and which may be sublimed, without, however, forming the corresponding anhydride.

The *dimethyl ester* melts at 67°–68° (Baeyer, Ber. 1898, 31, 1404), and the *diethyl ester* at 11·5° (cf. Perkin, Chem. Soc. Trans. 1896, 69, 1238, for physical properties).

It forms a *hydrazide*, m.p. 220°, by heating with hydrazine hydrate in absolute alcohol (Davids, J. pr. Chem. [ii.] 54, 74), and also an *azide*, $C_6H_4(CON_3)_2$.

HYDRO-ISOPHTHALIC ACIDS.

These acids are chiefly due to the work of Perkin and Pickles (Chem. Soc. Trans. 1905, 87, 293) and Perkin and Goodwin (ibid. 843).

The *dihydro-isophthalic acids* are not well known. The $\Delta^{1,4}$-acid, m.p. 270°, has been obtained from 1 : 3-dibromo-trans-hexahydro-isophthalic acid by the agency of potash ; and the $\Delta^{2,4}$-*dihydro-acid*, m.p. 255°, is also described as obtained in a similar manner from the 3 : 4-dibromohexahydro acid, but the constitution of these two acids is still regarded as unsettled.

All the four possible *tetrahydro acids* have been isolated. iso-Phthalic acid on reduction with sodium amalgam yields two acids, Δ^3 and the cis-form of Δ^4. Δ^3-*Tetrahydro-*

isophthalic acid melts at 168°, is

very soluble in water, and its anhydride melts at 78°. By the agency of caustic potash or hydrochloric acid it yields the sparingly soluble

Δ^2-*tetrahydroisophthalic acid*

m.p. 244°, which gives, with acetic anhydride, the anhydride of Δ^3-acid, m.p. 78°.

Cis-Δ^4-tetrahydroisophthalic acid

is isolated from the original reduction product, as stated above. It melts at 165°, is very soluble in water, and is easily converted into the *trans-acid* with concentrated hydrochloric acid. This trans-form is sparingly soluble, and melts at 227°.

Cis- and *trans-hexahydroisophthalic acids*, m.p. 163° and 148° respectively, were obtained synthetically by Perkin and Prentice (Chem. Soc. Trans. 1891, 59, 808; cf., however, Perkin and Goodwin, Chem. Soc. Trans. 1905, 87, 843), who condensed trimethylene bromide with sodio-methylene-malonic ester—

with sodium amalgam in alkaline solution. The *methyl ester* melts at 130°.

Δ^{1,8}-*dihydroterephthalic acid* is

prepared indirectly from the dibromide of Δ^2-tetrahydroterephthalic acid by the action of methyl alcoholic potash. Its *methyl ester* melts at 85°. In accordance with Thiele's view of the reduction of conjugated double linkings, it reduces to Δ^2-tetrahydroterephthalic acid.

Δ^1- *Tetrahydroterephthalic acid*

is prepared by boiling 1 part of terephthalic acid in caustic soda for 40 hours, and gradually adding 100 parts of sodium amalgam (4 p.c.). It melts above 300°; the *methyl ester* melts at 39° (Baeyer, Ber. 1886, 19, 1805; Annalen, 1888, 245, 160; 1890, 258, 32).

*Trans-*Δ^1-*tetrahydroterephthalic acid*

melts about 220°, and is obtained from the Δ^{1,5}-dihydro acid or from the dibromo-Δ^{1,3}-acid by reduction. The *methyl ester* melts at 3°.

*Cis-*Δ^2 *tetrahydroterephthalic acid* is formed together with the trans-form by reducing the Δ^{1,4}-dihydro-acid with sodium amalgam in the cold.

Trans-hexahydroterephthalic acid

is formed on heating the tetrahydro acids with aqueous hydriodic acid at 240°. It melts at 300°; its *methyl ester* melts at 71° (Baeyer, Ber. 1886, 19, 1806; Annalen, 1888, 245, 170; 1889, 251, 257). Its synthesis has been accomplished by Mackenzie and Perkin (Chem. Soc. Trans. 1892, 61, 174).

The *cis-* form, m.p. 162°, is obtained by reducing the very soluble bromo-hexahydro-terephthalic acid with zinc dust and acetic acid. Its methyl ester does not crystallise.

2 : 5-dichloroterephthalic acid has been prepared by Bocchi (Gazz. chim. ital. 26, ii. 406) from the dichlorocymene by oxidation with nitric acid.

Terephthalic aldehyde is prepared exactly as described in the case of phthalic aldehyde (Annalen. 1906, 347, 110). It exists as long needles, m.p. 116°.

PHTHALIC ANHYDRIDE *v.* PHTHALIC ACID.

PHTHALIDE *v.* LACTONES.

PHYCITE. Identical with erythrol (*q.v.*).

PHYSOSTIGMINE *v.* ORDEAL BEAN; also VEGETO ALKALOIDS.

PHYTIN, *inositol phosphoric acid*

$$C_6H_6(PO_4H_2)_6,$$

occurs in many plant seeds, usually as the calcium-magnesium salt. In bran, in the seeds of red-fir, peas, beans, pumpkin, red and yellow lupin, and in the potato and other tubers and bulbs, the greater part of the phosphorus exists in this form (Patten and Hart, Amer. Chem. J. 1904, 31, 564).

It occurs to the extent of 2 p.c. in wheat bran and 8 p.c in rice-bran (Suzuki and others, Bull. Coll. Agric. Tokyo. 1907, 7, 495), and is prepared from the latter by extraction with 0·2 p.c. hydrochloric acid. It is purified by precipitating with magnesia, washing the preparation, dissolving in acid and decolourising with charcoal, and again precipitating with magnesia (Contardi, Atti. R. Accad. Lincei. 1909, [v.] 18, i. 64). It is soluble in water and dilute alcohol; insoluble in benzene, ether, &c.; it does not crystallise (Posternak, Compt. rend. 1903, 137, 337 and 439). In plants it is associated with an enzyme, *phytase,* by which it is hydrolysed into inositol and phosphoric acid; this hydrolysis can also be brought about by dilute acids or by 20 p.c. caustic soda at 220° (Winterstein, Zeitsch. physiol. Chem. 1908, 58, 118; *see* also Neuberg, Biochem. Zeitsch. 1908, 9, 557; Levene, *ibid.* 1909, 16, 399; Neuberg, *ibid.* 1909, 16, 406).

The solution of the pure acid is stable and, when administered to animals by the mouth, has no ill effects (Mendel and Underhill, Amer. J. Physiol. 1906, 17, 75); 35 p.c. is absorbed by the organism, the remainder being eliminated as inorganic phosphates (Horner, Biochem. Zeit. 2, 428).

PHYTOSTEROL (phytosterin)

$$C_{26}H_{44}O,H_2O, \text{ or } C_{27}H_{46}O$$

is vegetable cholesterin (Hesse, Annalen, 1872, 192, 175). It is contained in calabar beans, in the bark of *Hamamelis virginiana* (Linn.) (Grüttner, Arch. Pharm. 1898, 236, 278); in the bark of *Berberis ;* in *Ergot,* in the leaves of *Eriodictyon crassifolium* (Benth.) (Power and Tutin, Pharm. Rev. 1906 24, 300) ; in prunas bark (Finnemore, Pharm. J. 1910, [iv.] 31, 604); in the dried rhizome and roots of the yellow jasmine (Moore, Chem. Soc. Trans. 1910, 2226), and of the *Cimcifuga racemosa* (Nutt.) (Finnemore, Pharm. J. 1910, [iv.] 31, 142); in the lichen, *Endocarpon miniatum* (L.) Ach. (Hesse, J. pr. Chem. 1898, [ii.] 58, 465); in wheat germs, in the wild cherry bark, in rape oil, in cocoanut, cottonseed, and in nearly all vegetable oils, and in various lamp oils (Marcusson, J. Soc. Chem. Ind. 1901, 484). It has also been found, probably in the form of esters, in certain peaty soils (Schreiner and Shorez, Chem. News, 1912, 105, 40). *See* also Kerstein (Chem. Zentr. 1899, ii. 91); Mügge (Zeitschr. Nahr. Genuss. 1898, 1, 45); Schmidt and Kerstein (Arch. Pharm. [iii.] 28, 49); Matthes and Rohdich (Ber. 1908, 41, 19, 1591); Matthes and Ackermann (*ibid.* 2000); Cohen (Arch. Pharm. 1908, 246, 51

A *hydrazine picrate* $C_6H_2(NO_2)_3OH.N_2H_4$ is described by Silberrad and Phillips (Chem. Soc. Trans. 1906, 93, 474). Picric acid stains may be removed by a solution of alkaline sulphide or polysulphide, followed by a thorough washing with soap and water (Bougault, J. Pharm. Chim. 1903, 18, 155).

Detection and estimation. Picric acid is not volatile in steam, and can readily be detected by its bitter taste and the sparing solubility of

without action upon other pigments, with the exception of the lakes, and is only very slowly attacked by sulphuretted hydrogen. Aureolin is permanent in water-colour, as well as in oils.

Cobalt pink, magnesia-cobalt pink, is produced when a thin paste of finely divided magnesium carbonate together with an aqueous solution of cobalt nitrate is dried, and subsequently ignited in a covered vessel at a high temperature. Strongly ignited cobaltous arsenate and phosphate are also of a pink or foxglove-red colour, inclining to violet. These pigments are sometimes known as '*cobalt red*' or '*cobalt violet*.'

Rinmann's green, Cobalt green, sometimes termed *zinc green*, cobalt zincate, $CoOZnO$, is a delicately shaded and artistically satisfactory pigment, of great permanence, and innocuous to other colours. The best product is obtained by drying and calcining zinc oxide, previously made into a paste with an aqueous solution of cobalt nitrate, sulphate or chloride. Another cobalt green is prepared by mixing zinc and cobalt solutions with sodium phosphate, and igniting the washed and dried precipitate. The product so obtained has a bluer tint than the true Rinmann's green.

Turquoise green, chrome-alumina cobalt oxide, is a bluish-green pigment mostly used in ceramic painting, but occasionally also in oils. It is made by heating to redness aluminium and chromium hydroxides together with cobaltous carbonate.

Cobalt blue, Thénard's blue, Leyden blue, King's blue, cobalt ultramarine, Gahn's ultramarine, azure blue, &c. Several methods are used in the production of cobalt blue. The variety of this pigment known as Wenzel's blue can be prepared by adding ammonia to a solution of cobalt chloride, mixing the precipitated and washed hydroxide with alumina, drying, and igniting; or by moistening recently precipitated aluminium hydroxide with a solution of cobalt nitrate, drying the mixture, and strongly igniting it. Another cobalt blue is made by mixing freshly precipitated and washed cobalt phosphate with newly precipitated and washed aluminium hydroxide. The mass is dried, ignited, and ground. Cobalt arsenate may be ·substituted for the phosphate. Also a mixture of alum and cobalt nitrate solutions may be precipitated by sodium carbonate, the precipitate being washed, dried, and ignited, as usual. It will be seen that cobalt blue may be a cobalt aluminate or a compound of the phosphate or arsenate of cobalt with alumina.

These cobalt pigments are permanent, except in the presence of ammonium sulphide. They are available in all media, including fresco, and are without action upon other pigments. The tint of the blue is slightly greenish, and in artificial light a shade of violet is perceptible. Cobalt blue is especially valuable in water-colour, for which it is somewhat more suitable than for painting in oils.

Leitch's blue, or *cyanine blue*, is a 'mixed' pigment, composed of cobalt blue and Prussian blue. It is moderately durable, but presents no very striking advantages. As Prussian blue is a constituent, this pigment cannot be used in fresco work.

Smalt, Saxon blue, cobalt-potassium silicate, is a deeply coloured glass which, in a fine state

of division, was at one period much used as a pigment. Artificial ultramarine has, to a great extent, replaced it. Smalt is deficient in chromatic and covering power, but it is perfectly durable and without injurious effect upon any other pigments.

Cæruleum, Cerulean blue, Cœlinblau, Bleu céleste, cobalt stannate, is a greenish-blue, permanent, semi-opaque colour, made by igniting stannic oxide, previously moistened with a solution of cobaltous nitrate. It possesses the advantage of appearing less violet by artificial light than the other cobalt blues.

Cobalt brown results when cobaltous sulphate, ferrous sulphate, and ammonium sulphate, or ammonia alum, are very strongly heated together. Another method of manufacture is to mix ferric oxide with aluminium hydroxide and a cobaltous salt, the mixture being then ignited.

Pigments containing manganese. *Manganese green, Cassel green*, barium manganate, is made by cautiously heating a mixture of manganese nitrate or oxide with barium nitrate. Or, manganese dioxide and carbonate may be heated with barium peroxide. Another manganese green (Böttger's) is made as follows. A solution of manganese chlorate is precipitated by barium nitrate. The violet compound produced is washed, dried, mixed with barium hydroxide and carefully heated. A green mass results, which requires washing with water and further treatment.

Manganese blue. A mixture of kaolin, manganese oxide and barium nitrate, or of silica, manganese oxide and barium nitrate, ignited at a red heat, is stated to yield a blue product, available for use as a pigment. Soda ash, silica, calcium carbonate, and manganese oxide, mixed together and calcined, yield a similar product.

Manganese violet, mineral violet, permanent violet, impure manganese metaphosphate, is prepared by evaporating to dryness a mixture of solutions of phosphoric acid and manganous chloride, fusing the residue, boiling with ammonium carbonate solution, allowing the turbid liquid to stand, filtering, evaporating the filtrate to dryness, fusing the residue, pulverising it and boiling with water. The pigment separates as a fine violet precipitate, which must be collected on a filter, washed, and dried.

Raw umber, Turkey umber, Levant umber, Terra ombra, is a greenish- to yellowish-brown, silicious and ferruginous earth, containing a considerable proportion of one or other of the higher oxides of manganese, Mn_3O_4 and MnO_2. Most of the best specimens are of Cypriote origin, but many countries yield a supply of this natural pigment, which merely has to be ground, levigated, and dried at 100°. Raw umber is a permanent and justly-valued pigment. It has no injurious effect upon other stable colouring matters.

Burnt umber, Velvet brown, Chestnut brown, &c., result from the calcination of raw umber; they are equally permanent, and can be used in conjunction with all other durable pigments. The colour of burnt umber is warmer and richer than that of the raw product.

Cappagh brown, mineral brown, euchrome, is a highly manganiferous and ferruginous earth,

PIMENTO. Pimento or Allspice is the dried, full-grown but unripe fruit of *Pimenta officinalis* (Lindl.).

The plant is indigenous to the West Indies and is largely cultivated in Jamaica, whence our supplies are derived. The globular berries, dark purple when fresh, brown when dry, are from 5 to 8 mm. in diameter. They are enclosed in a two- but sometimes one- or three-celled fruit. They are gathered when of full size but still not quite ripe, and dried in the sun.

The characteristic flavour is due to an aromatic, pungent, volatile oil, resembling in smell that of cloves; other important constituents being a fixed oil, tannin, resin, and much starch. Full analyses by Richardson (U. S. Dept. of Agric., Div. of Chem. Bull. 13, 221) yielded the following results :—

	Whole	Ground Max.	Min.
Water	6·19	8·82	5·51
Ash	4·01	5·53	3·45
Volatile oil . .	5·15	3·32	2·07
Fixed oil . .	6·15	6·92	3·77
Fibre	14·83	18·98	13·45
Proteid	4·38	5·42	4·03
Nitrogen . . .	0·70	0·87	0·64
Quercitannic acid (' tannin equivalent ') . .	10·97	12·74	8·27

Uses. Pimento finds its chief use as a condiment, but it is *officinal* in the British Pharmacopœia together with an *aqua* and the essential oil. Its therapeutic action is that of an aromatic stimulant and carminative.

Adulteration. Comparatively little is sold in the ground state in this country, so that pimento is rarely if ever adulterated here. Very few samples, however, are examined under the Sale of Food and Drugs Acts. The usual spice adulterants may be looked for, namely, added starches, ground olive stones, and the shells of coconut and almond, &c.

Analysis. Microscopical examination will suffice to detect all the likely adulterants of vegetable origin. The most characteristic structures to be observed are minute starch grains, usually about 8μ in diameter and not exceeding 12μ, with a distinct hilum, often joined in pairs or triplets, or larger aggregates : numerous colourless stone cells, some very large ; and pigment cells containing irregular port wine or amber-coloured masses of resin or gum.

The most useful determinations are ash, tannin, and fixed ether extract. Unless adulteration is discovered by the microscope, anything further is seldom required. Should olive stones or nutmeg be suspected of being present, their special characters are given under PEPPER (*q.v.*).

The direct determination of tannin is neither easy nor satisfactory, but very fair results may be obtained by calculating the 'quercitannic acid from the proportion of oxygen absorbed from potassium permanganate.

The process, due to Richardson (U. S. Dept. of Agric., Div. of Chem. 13, 167), is as follows : Boil 2 grms. of the sample, after thoroughly extracting with ether, with 300 c.c. of water for 2 hours, cool, make up to 500 c.c. with water and filter. Mix 25 c.c. of the filtrate with 750 c.c. of water, add 25 c.c. of indigo solution (made by dissolving 6 grms. of potassium sulphindigotate in hot water, cooling, adding

50 c.c. of sulphuric acid (conc.) and making up to 1 litre). Then titrate with the permanganate solution (1·333 grms. per litre) until the liquid becomes of a bright yellow colour. Note the number of c.c. used. Ascertain the equivalent of the permanganate in terms of N/10 oxalic acid and calculate the number of c.c. of the former used in oxidising the pimento solution. Convert this into its equivalent number of c.c. of oxalic acid. Each c.c. of the oxalic acid =0·0623 grm. of quercitannic acid.

The following table will afford some idea of the figures yielded by genuine samples, but comparatively few analyses of authentic specimens are on record.

Analyses by Winton, Ogden and Mitchell, Ann. Rep. Connect. Agricult. Station, 1898, p. 204.

	Max.	Min.	Average
Moisture . . .	10·14	9·45	9·78
Ash	4·76	4·15	4·47
„ soluble in water	2·69	2·29	2·47
„ insol. HCl .	0·06	0·00	0·03
Ether extract, volatile	5·21	3·38	4·00
„ „ fixed	7·72	4·35	5·84
Alcohol extract .	14·27	7·39	11·79
Starch (diastase method) .	3·76	1·82	3·04
Fibre	23·98	20·46	22·39
N.	1·02	0·83	0·92
Quercitannic acid .	12·48	8·06	9·71

Standards. The United States standard for Allspice provides that the quercitannic acid shall not be less than 8 p.c., the ash not more than 6 p.c., the ash insoluble in HCl not more than 0·5 p.c. and the fibre (which should be determined as in pepper) (*q.v.*) not more than 25 p.c. C. H. C.

PIMENTO OIL *v.* OILS, ESSENTIAL.

PINACHROMY and **PINATYPE.** Processes of colour photography devised by E. Koenig (*v.* J. Soc. Chem. Ind. 1906, 657).

PINCHBECK. An alloy of zinc and copper brought into notice by Christopher Pinchbeck in the latter part of last century. It was formerly much employed in the making of watchcases, and other small ornamental articles in imitation of gold. Its composition is variable, but usually consists of 9 parts of copper to 1 part zinc.

PINE-APPLE. The fruit of *Ananas sativus* (Schult.) [*Bromelia ananas*] a tropical plant, grown largely in the West Indies, Singapore, Florida, the Bahamas, Natal, and other hot countries. According to Munson and Tolman (J. Amer. Chem. Soc. 1903, 25, [iii.] 272), the average composition (38 samples) of fresh pine-apples, 21 from Florida, 10 from Cuba, 4 from Porto Rico, 2 from the Bahamas, and 1 from Jamaica, is

Water	Pro- te·n	Free acid (as H_2SO_4)	Reducing sugar	Cane sugar	Ash	Insoluble matter
85·83	0·42	0·60	3·91	7·59	0·40	1·52

In different specimens, the reducing sugars varied from 1·76 to 9·75 p.c. ; the cane sugar from 3·0 to 10·5 p.c. According to Lindet (Bull. Soc. chim. 1884, 40, 65), pine-apples contain 1 p.c. or more of mannitol. Pine-apple juice is said to contain an enzyme, *bromelin*, which resembles pepsin and can digest a thousand times its weight of proteids in a few hours. It can be precipitated from the juice by the addition of common salt, and can operate in acid,

Egyptian asphalt contains :

	p.c.
Carbon	85·29
Hydrogen	8·24
Oxygen	6·22
Nitrogen	0·25

The ·bitumen of Judea, found floating on the Dead Sea, contains :

	p.o.
Carbon	77·84
Hydrogen	8·93
Oxygen	11·54
Nitrogen	1·70

Sulphur is invariably present in natural bitumens, varying in quantity from 3 to 4·2 p.c. and even 10 p.c. ; from such samples, hydrogen sulphide is always given off on heating. Asphaltums and bitumens vary considerably in character. Generally, their appearance is that of smooth, hard, brittle, black, or brownish-black resin, breaking with a distinct conchoidal fracture : the sp.gr. varies from 1 to 1·7; when free from mineral matter they may be even lighter than water. When distilled with water, asphaltum yields a volatile oil called by Boussingault 'petrolene,' probably consisting of a mixture of paraffins. The residue of 'asphaltine,' which remains when the petrolene is completely driven off, is a solid black substance resembling the original substance prior to distillation, but which does not soften below under about 300°, and decomposes below its fusing point.

Trinidad pitch yields, when heated—

	p.c.
Volatile organic matter	76·75
Non-volatile organic matter	17·77
Ash	5·48
	100·00

Natural bitumen is only partially soluble in alcohol, but more completely so in carbon disulphide, carbon tetrachloride, petroleum spirit, chloroform, oil of turpentine, coal-tar, benzene and naphthas ; the pyridine bases, also derived from coal-tar, scarcely act upon it. The portion, however, that passes into solution communicates a strong greenish fluorescence to the liquid, and when examined spectroscopically, in the manner described for examining crude anthracenes for certain impurities (Chem. News, 26, 199 ; 31, 35, 45), two distinct absorption bands are visible near the D line of the spectrum, from yellow to green, which distinguishes it from all other pitches, coal-tar excepted, which occasionally shows bands, but invariably situated in the blue portion of the spectrum near the F and G lines.

In petroleum spirit, 74·23 p.c. of its organic matter is soluble and 20·29 p.c. insoluble.

At a temperature varying from 58° to 60° bitumen softens, and it melts at about 100°, although varieties are met with that melt only at a much higher temperature.

The following table of results obtained by A. E. Jordan and given in Allen's Organic Analyses shows the difference between natural asphalts and artificial products.

Material.	Ash.	Organic matter.		Action of petroleum spirit.		
		Volatile.	Non-volatile.	Soluble.	Insoluble.	Percentage of organic matter soluble.
Asphalt (origin unknown)	0·60	80·79	18·61	47·63	51·77	47·91
Trinidad pitch	5·48	76·75	17·77	74·23	20·29	78·53
Petroleum pitch	none	50·43	49·57	36·16	63·84	36·16
Shale oil pitch	0·25	66·40	33·35	63·62	36·13	68·77
Coal-tar pitch	0·15	49.33	50.52	18.56	81.29	18·58
Bone pitch (inferior)	0·33	56·15	43·52	29·96	69·71	30·05

Boussingault's methods are not now used and the terms petrolene and asphaltene used by him have received another significance, that portion soluble in petroleum spirit, ether, or acetone being known as petrolene and the portion insoluble in any of these liquids but dissolved by boiling turpentine or cold chloroform being known as asphaltene.

Applications of asphaltum. — The purer asphaltums are employed almost exclusively for the manufacture of black varnishes and japans, for which purpose they are eminently adapted, yielding surfaces and coatings of great brilliancy and not prone to ' break up ' or disintegrate. Asphaltum selected for the purpose of the varnish maker should be practically free from mineral matter or within a limit of 5 p.c., it should be completely soluble in carbon di-

sulphide, chloroform, high boiling coal-tar naphtha. and oil of turpentine (mineral matter excepted). It should break with a conchoidal fracture and brilliant lustre. It should not flow or lose shape, like wood tar and many of the fatty pitches. when left on a plane surface, and an angular fragment should retain its shape and the sharpness of its angles in boiling water.

Asphalt rock. Asphaltum is often met associated with sand or limestone or the two variously admixed ; in this condition the mineral is known as ' asphalt rock.' and occurs in the upper Jurassic formation interstratified with ordinary limestone.

The following figures, by Durant Claye, show the proximate composition of some rock asphalts employed for paving :—

	Val de Travers Switzerland.	Lobsann Alsace	Seyssel Ain France	Maestu Spain	Ragusa Sicily
Water and other matters volatilised at 100° C.	0·35	3·40	0·40	0·40	0·80
Bituminous matter	8·70	11·90	9·10	8·80	8·85
Sulphur in organic combination or free state	0·08	4·99	—	trace	—
Iron pyrites	0·21	4·44	—	—	—
Alumina and oxide of iron	0·30	1·25	0·05	4·35	0·90
Magnesia	0·10	0·15	0·05	3·85	0·45
Lime	49·50	38·90	50·50	5·70	49·00
Carbon dioxide	40·16	31·92	39·80	8·15	39·40
Combined silica	—	—	—	11·35	—
Sand	0·60	3·05	0·10	57·40	0·06
	100·00	100·00	100·00	100·00	100·00

Native calcareous asphalt exhibits a brown or nearly black colour and breaks without evidence of cleavage. The fracture is earthy and granular, not unlike chocolate, both in appearance and colour. When long exposed to the air it loses this character and then resembles ordinary limestone: this change, however, only extends to the surface.

The specific gravity of rock asphalt is about 2·23. It is hard and may be broken with a hammer, but when warmed it may be softened to a kind of paste and at about 60° falls to powder.

Good rock asphalt is homogeneous in structure and shows no indication of contained limestone. It is frequently veined, and contains large crystals of calcite impregnated with bitumen; this feature is considered an important indication, bad specimens or low qualities showing an absence of such impregnation, which renders them difficult to manipulate. Val de Travers, Seyssel, and other asphalt rocks, when employed for paving, are melted with definite proportions of good native material, such as Trinidad pitch. The product of this mixture is technically known as 'mastic,' and in using it further additions of bitumen, shale oil, and grit are frequently made.

The following analysis by Durant Claye will convey a general idea of these compositions:

	Refined bitumen from Bastennes	Imitation asphalt made from coal-tar
Moisture	0·30	0·60
Bituminous matters soluble in carbon disulphide	69·35	20·65
Organic matter insoluble in carbon disulphide	4·40	18·45
Alumina and oxide of iron	2·85	2·65
Magnesium and calcium carbonates	2·65	39·60
Silica	20·35	18·05
	100·00	100·00

For determining the actual bituminous matter in asphaltic rocks, natural and otherwise, the air-dried sample is exhausted with suitable solvents, which may consist of carbon disulphide, Russian oil of turpentine or coal-tar benzene. The operation may be conducted in a Soxhlet's tube, and if a correction be made for the moisture expelled at 100° the loss of weight furnishes the quantity of bitumen removed. The determination may be further checked by distilling off the solvent and weighing the residue, observing the usual precaution of drying at 100° until constant. The bitumen thus obtained should be heated further to 220°, when, if the sample is good, there will be little or no further loss of weight; if, however, volatile oils or petroleum be present, the loss may be considerable.

The volatile oil is best determined by repeatedly digesting the powdered sample with cold alcohol and weighing the residue; the exhaustion may be considered as complete when a portion of the alcoholic washing shows no turbidity on dilution with water.

If the residue left after exhaustion exhibits a dark colour, other organic constituents of valueless nature are present. Their proportion may be ascertained by igniting the weighed residue left after the removal of the bitumen, re-carbonating it with ammonium carbonate, again gently igniting it and re-weighing. The loss of weight represents the quantity of non-bituminous matter present.

Val de Travers asphalt gives up the whole of its organic matter to petroleum spirit, imparting a deep brown colour to the fluid, perfectly free from fluorescence, whereas the soluble portion of coal-tar pitch does not exceed 20 or 25 p.c., yielding a solution exhibiting a deep greenish fluorescence, a characteristic of this pitch in any of its solvents and which renders its detection alone or in admixture a matter of no great difficulty (v. infra).

Pitches derived from technical processes.

Artificial pitches. Coal-tar pitch may be looked upon as occupying the most prominent position in the series, both as regards the magnitude of its production and its corresponding consumption for the purposes of artificial fuel, asphalts and varnishes.

Some idea of the extent to which this residue is produced in the United Kingdom, together with the industry springing out of it, may be gathered from the statement that according to the last census of production the total output of

TABLE III.—ROTATION OF VARIOUS ESTERS DERIVED FROM GLYCERIC ACID.[1]

	A Glycerate $[\mathrm{M}]_D^{15}$	B Diacetyl-glycerate $[\mathrm{M}]_D^{15}$	A−B	C Dimethoxy-propionate $[\mathrm{M}]_D^{15}$	A−C
Methyl	−5·76°	−24·56°	18·8°	−103·8°	98°
Ethyl	−12·30	−35·56	23·26	−114·4	102·1
n-Propyl	−19·15	−45·17	26·06	−122·5	103·3
sec-Propyl	−17·49	−41·69	24·20	—	—
n-Butyl	−21·37	—	—	−124·2	102·8
isoButyl	−23·05	−50·88	27·33	—	—
n-Heptyl	−23·05	−47·89	24·84	−127·9	104·8
n-Octyl	−22·28	−47·92	25·64	−125·6	103·3

TABLE IV.

	$[\mathrm{M}]_D^{20}$
Menthyl formate	−146·3°
„ acetate	157·3
„ propionate	160·2
„ n-butyrate	157·1
„ n-valerate	157·3
„ n-caproate	157·7
„ n-heptylate	157·7
„ n-caprylate	155·8

TABLE V.—SECONDARY ALCOHOLS.

	$[\mathrm{M}]_D^{20}$
sec-Propyl-methyl-carbinol	+4·3°
„ ethyl „	15·4
„ n-propyl „	24·7
„ n-butyl „	33·3
„ n-amyl „	32·9
„ n-hexyl „	33·9
„ n-octyl „	34·5
„ n-decyl „	34·5

(Pickard and Kenyon, Chem. Soc. Trans. 1912, 101, 624).

With the above data several points may be illustrated.

1. Although ordinary malic acid in aqueous solution is lævorotatory like the esters derived from it, and is called l-malic acid, it is to be inferred from the behaviour of its concentrated solutions that the substance, if it could exist at the ordinary temperature in the liquid form, would show a positive rotation. Solutions of above $p=34$ have a positive rotation at 20°.

TABLE VI.—ROTATION OF ESTERS OF VARIOUS ACIDS [2] (temperature approximately 20°).

Ethyl	$[\mathrm{M}]_D$	Ethyl	$[\mathrm{M}]_D$	Ethyl	$[\mathrm{M}]_D$	Ethyl	$[\mathrm{M}]_D$
Lactate	−12·2°	Glycerate	−12·3°	Malate	−19·8°	Tartrate	+15·86°
Acetyl-lactate	−79·7	Diacetyl-glycerate	−35·6	Acetyl-malate	−52·3	Diacetyl-tartrate	+10·0
Benzoyl-lactate	+59·0†	Dibenzoyl-glycerate	+89·2	Benzoyl-malate	−11·4	Dibenzoyl-tartrate	−123·6
Methoxy-propionate	−118·9	Dimethoxy-propionate	−114·4	—	—	—	—

Methyl		Methyl		Methyl		Methyl	
Lactate	−8·6	Glycerate	−5·8	Malate	−11·1	Tartrate	+3·8
Methoxy-propionate	−112·7	Dimethoxy-propionate	−103·8	Methoxy-succinate	−92·4	Dimethoxy-succinate	+180·0†

Tartaric acid, Table II., behaves similarly, but in an opposite sense, for although it itself and its salts in aqueous solution as well as its simple esters in the homogeneous state, have a positive rotation and it is called d-tartaric acid, it would nevertheless give, if it could exist in the liquid homogeneous condition, a negative rotation.

2. Although to the names of many compounds the letters d- and l- are prefixed merely to indicate the sign of their rotation, Emil Fischer has been able to trace a genetic relationship between many substances related to the sugars, and prefixes the letters d- and l- to the names of compounds according to the structural relationship which they bear to glucose. In a long series of researches, pre-eminent alike for manipulative skill and reasoning power, Fischer has shown that natural glucose must have one or other of the structural formulæ:

[1] For references see P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 865.

[2] From P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 867, which see regarding data marked thus †.

```
     CHO              CHO
      |                |
 H—C—OH          HO—C—H
      |                |
 HO—C—H          H—C—OH
      |                |
 H·C—OH           HO—C—H
      |                |
 H·C—OH           HO—C—H
      |                |
   CH₂OH            CH₂OH
 d-Glucose.        l-Glucose.
```

and as it is hardly probable that we shall ever be able finally to discriminate between these, he has made the above arbitrary selection. d-Tartaric acid must then be, as he has shown,

```
      COOH
       |
  H—C—OH
       |
 HO—C—H
       |
      COOH
  d-Tartaric acid.
```

the two upper asymmetric carbon atoms of the

rapidly with diminution of concentration, the rate becoming greater as the dilution increases, to attain ultimately to a value of $-20°$.

Thus the rotation of this ester, whose specific rotation in the pure condition is only $+7·8°$, can be made to vary from $+41°$ to $-20°$ by

Influence of Various Solvents on the Rotation of Ethyl Tartrate.

Fig. 36.

solution in these solvents; clearly, therefore, care must be taken in reporting the exact circumstances under which any rotation has been measured, and also in utilising rotation data obtained by the use of several different solvents. The curves also show that if an active compound is solid, so that its rotation in the homogeneous liquid condition cannot be determined, this value may still be arrived at by extrapolation from the data for its solutions, preferably in a number of solvents, the accuracy with which the extrapolation could be made depending, of course, on the solubility of the compound.

Many attempts have been made to explain these remarkable effects. Naturally a correlation has been suggested between the rotation and the osmotic molecular weight of the dissolved substance, but it has proved impossible up to the present to establish any connection. (See Frankland and Pickard, Chem. Soc. Trans. 1896, 69, 131; Patterson, ibid. 1901, 79, 182; 1902, 81, 1111; Ber. 1905, 38, 4049; 1908, 41, 113; Patterson and Thomson, ibid. 1907, 40, 1244; Walden, ibid. 1905, 38, 389; 1906, 39, 658; 1907, 40, 2463; Purdie and Irvine, Chem. Soc. Trans. 1904, 85, 1055.)

Another proposal, originally made by Tammann, was that the rotation depends upon the internal pressure of the solvent or of the mixture of solute and solvent. This idea was applied by Patterson (Chem. Soc. Trans. 1901, 79, 188) in the case of ethyl tartrate in various solvents, but instead of calculating the internal pressure,

the molecular solution-volume of the ethyl tartrate at infinite dilution in the different solvents was determined, the assumption being made, as a first approximation, that all the change of volume suffered in the process of solution might be attributed to the solute, and further, that the magnitude of the solution-volume might be regarded as a measure of the internal pressure. Although these assumptions are not generally admissible, it is nevertheless possible that in some instances they may be nearly fulfilled. In any case experiment discovered a parallelism between the magnitude of the specific rotation and the molecular solution-volume, both at infinite dilution, as is illustrated in the following table (Ber. 1905, 38, 4101).

TABLE X.—ROTATION AND SOLUTION-VOLUME OF ETHYL TARTRATE IN VARIOUS SOLVENTS.

(Ethyl tartrate, M.V.$=170·9$ c.c.)

Solvent	$[M.S.V.]^{20}$ infinite dilution	$[\alpha]_D^{20}$ infinite dilution
Water . .	160·1	$+26·85°$
Methyl alcohol .	159·3	$+11·50$
Glycerol . .	163·3	$+10·57$
Ethyl alcohol .	164	$+9·13$
n-Propyl alcohol	167·5	$+7·40$
iso-Butyl alcohol	170·3	$+6·53$
sec-Octyl alcohol	174·3	$+5·24$
Benzene . .	175·1	$+6·1$
Toluene . .	174·8	$+4·6$
o-Xylene . .	176·8	$+2·7$
m-Xylene . .	176·5	$+1·8$
p-Xylene . .	176·1	$+0·7$
Mesitylene .	177·4	$-3·0$
Chloroform .	178	$-3·2$

Excepting for water, there appears to be a fairly close relationship between the values of these two magnitudes. The idea was taken up by Winther and applied to explain the change of rotatory power with variation of temperature. In certain cases it is found that there is a direct, linear relationship between the values of the rotation and the molecular volume either in the homogeneous condition or in solution. Thus, for example, the figures for homogeneous ethyl diacetyltartrate may be given.

TABLE XI.

t	$[\alpha]_D$	$\Delta[\alpha]_D$	v	Δv	k
56·8°	$+4·37°$	0·38	0·8906	0·0087	44
67·6	4·75	0·17	0·8993	0·0027	63
71·3	4·92	0·28	0·9020	0·0061	46
78·2	5·20	0·40	0·9081	0·0070	57
86·7	5·60	0·70	0·9151	0·0114	61
100	6·30		0·9265		

In the above table v is the specific volume, and k is a constant calculated from the equation:

$$\Delta[\alpha]_D = k\Delta v.$$

The values of k vary irregularly about a mean value of 54, so that the rotation appears to be directly proportional to the specific volume. (For many other examples see Winther, Zeitsch. physikal. Chem. 1906, 55, 263.)

Muta-rotation. It not infrequently happens that the rotation of a compound, generally in

some property irrespective of the chemical composition of the solvents. It is interesting that, whilst the maximum rotation of the homogeneous ester lies at a temperature of 175°, it is again quite apparent in a solution in m-dinitro-benzene of p=49·6, but at a lower

Influence of Temperature on Rotation in Solution
Ethyl Tartrate in Various Solvents.

Fig. 37.

temperature, 123°. The curve for p-nitro-toluene, p=20, shows a maximum at about 85°, and, from the appearance of the other curves, the maximum passes rapidly to lower temperatures as the rotation increases. It seems likely that other substances closely related to ethyl tartrate would behave in solution in a very similar manner.

Rotation of active salts in solution. In 1873, Landolt (Ber. 1873, 6, 1077) observed that some of the neutral tartrates in aqueous solution had all very nearly the same specific rotation, whilst, later, Oudemans (Annalen, 1879, 197, 48, 66) showed that the rotation of dilute solutions of salts of quinamine seemed to be independent of the acid radicle. Hädrich (Zeitsch. physikal. Chem. 1893, 12, 476) applied the dissociation theory to the explanation of these results, suggesting that, as the solution of a salt is diluted, the rotation is modified because the active radicle becomes more and more dissociated from, and therefore less and less influenced by, the inactive radicle. In very dilute solutions, the rotation is that, merely, of the free active ion. Thus Landolt found the following data for solutions containing 7·69 grms. of tartaric acid in 100 c.c. Even in these by no

means very dilute solutions the rotations lie fairly close together.

Neutral tartrate of	$[M]_D$
Lithium	+58·1°
Sodium	59·9
Potassium	64·4
Ammonium	63·0

Again, Pope and Peachey (Chem. Soc. Trans. 1899, 75, 1086) give the following rotations for compounds formed by the combination respectively of dextro- and lævo- tetrahydroquinaldine with dextro-camphor-sulphonic acid.

Substance	$[M]_D$
$dC_{10}H_{13}N \cdot dC_{16}H_{15}O \cdot SO_3H$	+173·3°
l —————— $\cdot l$ ——————	−69·5

Half the difference between these, 121·4°, should be the rotation of a dilute solution of either form of tetrahydroquinaldine hydrochloride, and for the lævo variety experiment gave −121·7°. Further, half the sum of the above, 51·9°, should be the rotatory power of ammonium camphor sulphonate, for which the value 51·7° was found. Use is occasionally made of this principle in determining the rotation of small quantities of active bases or acids, obtained by the resolution of potentially active compounds.

The truth of this Law of Oudemans, as it is called, has been questioned by F. L. Shinn (J. Phys. Chem. 1907, 11, 201).

The following table gives some data for ethyl tartrate and for nicotine, in regard to the relative effect of the same set of solvents on the rotation of a number of different active compounds.

TABLE XII.

Solvent	Ethyl tartrate $[a]_D$ infinite dilution	Nicotine $[a]_D$ infinite dilution
Formamide .	+30·4°	−70°
Water .	26·85	77·4
Methyl alcohol .	11·5	129·4
Ethyl alcohol .	9·13	140·1
Benzene .	6·1	163·5
Ethylene bromide	−19·1	183·5

The sequence of the rotations in these different solvents is the same for both active compounds. *See also* Walden (Ber. 1905, 38, 345) for data bearing on this subject. Further work in this direction is desirable.

Mixed solvents. The effect of mixed solvents such, for instance, as a mixture of nitrobenzene and ethylene bromide on ethyl tartrate, or of water and calcium chloride on glucose, has been examined by Rimbach (Zeitsch. physikal. Chem. 1892, 9, 698; Rimbach and Weber (*ibid.* 1905, 51, 473); Patterson and Montgomerie (Chem. Soc. Trans. 1909, 95, 1128); Stubbs (*ibid.* 1911, 99, 2265); Patterson and Anderson (*ibid.* 1912, 101, 1833), but no generalisation seems to be possible as yet.

Combination of Active Solute with Inactive Solvent.

A suggestion often made to account for the variations of rotation observed in solution in what are termed 'indifferent' solvents, is that complex molecules of solute and solvent are formed, but the evidence advanced is usually of a negative character. An extensive research

POLIANITE r. Pyrolusite.

POLONIUM *Radium F : Radiotellurium.* At. w. = approx. 210 ?.

A radioactive element, discovered by P. and M. Curie in the residue obtained from pitchblende after the mineral had been roasted with sodium carbonate and the product extracted with sulphuric acid to dissolve uranium salts. The insoluble residue, from which radium was originally prepared, was found to contain another radioactive element which was precipitated together with bismuth sulphide by sulphuretted hydrogen in acid solution (Compt. rend. 1898, 127, 175). The further separation of the active body from bismuth was effected by the following methods: (1) sublimation of the sulphides at 700° in vacuo, the active sulphide being the more volatile; (2) precipitation of the basic nitrates from solution, the active material precipitating first; (3) precipitation of a strongly acid chloride solution with hydrogen sulphide, the active sulphide separating first. (For the preparation of polonium compounds r. also Giesel, Ann. Chim. Phys. 1899, [ii.] 69, 91; Ber. 1902, 35, 3608; 1903, 36, 728, 2368; 1906, 41, 1059; Marckwald, Ber. 1902, 35, 2285; Curie and Debierne, Compt. rend. 1910, 150, 386.)

In 1902, Marckwald (Ber. 1902, 35, 2285, 4239; 1903, 36, 2662) obtained a radioactive substance associated with tellurium, which he called radiotellurium. This is almost certainly identical with polonium, as Debierne soon afterwards pointed out (Compt. rend. 1904, 139, 281). Although Marckwald (Jahrb. Radioaktiv. Elektronik. 1905, 2, 133) disputed their identity, he subsequently (Chem. Zentr. 1906, ii. 412) recommended that his material should be called polonium.

Polonium has been found in the uranium mineral carnotite (Friedel and Cumenge, Compt. rend. 1899, 128, 532).

When a plate of bismuth is immersed in a polonium solution, the active matter is deposited on the plate; the active material is also precipitated by stannous chloride (Marckwald).

The radiation from polonium is extremely active, consisting entirely of α-rays identical with those of radium (Becquerel, Compt. rend. 1903, 136, 431, 977). The rays are deflected in a strong magnetic field (Mackenzie, Phil. Mag. 1905, [vi.] 10, 538; Ewers, Chem. Zentr. 1906 i. 1084). The range of the α-particles in air is 3·8 cm. (Levin, Amer. J. Sci. 1906, [iv.] 22, 8 · cf. Aschkinass, Annalen Physik. 1908, [iv.] 27, 377). The activity of polonium decays according to the usual exponential law, the half-period being 140 days (Curie, Compt. rend. 1906, 142, 273). The half-period for radiotellurium is 139·6 days (Greinacher and Herrmann, Jahrb. Radioaktiv. Elektronik. 1905, 2, 136).

Owing to the minute quantities of polonium available it has been extremely difficult to detect helium as one of its disintegration products, but Curie and Debierne (Compt. rend. 1910, 150, 386) have obtained 1·3 c.mm. of helium from approximately 0·1 mgm. of polonium (cf. Greinacher and Kernbaum, Zeitsch. physikal. Chem. 1907, 8, 339). The spectrum lines λ=4642, 4170·5, 3913·6, 3652·1 probably belong to polonium. Polonium preparations slowly evolve heat (Duane, Compt. rend. 1909, 148, 1665).

Polonium has been identified with radium F, the last of the series of transformation products of radium that has been recognised. The change from radium to radium F involves the loss of four α particles from the atom. The atomic weight of polonium should therefore be about 210. The unknown radium G, into which polonium disintegrates, is devoid of sensible radioactivity, since the half period of polonium preparations that have been kept for five years is practically identical with the figure given above (Waters, Phil. Mag. 1910, [vi.] 19, 905). Radium G will probably prove to be lead.

The radio-lead of Hofmann and Strauss (Ber. 1901, 34, 3033: Hofmann and Wolff, ibid. 1903, 36, 1040 has been shown to owe its activity to the presence of the transformation products radium D. E and F. The substance β-polonium, described by Giesel (Ber. 1906, 39, 780) was shown later to be radium E (Giesel, ibid. 1906, 39, 1014).

POLYBASITE. A sulphantimonite of silver (60-72 p.c. and copper (3-15 p.c.) with the formula 8 Ag₂Cu₂S·Sb₂S₃ S, (F. R. Van Horn, Amer. J. Sci. 1911, 32, 401. The antimony may be partly or wholly replaced by arsenic, forming a passage to the isomorphous species pearceit: small amounts of zinc and iron are also often present. Both minerals occur as iron-black, six-sided plates with monoclinic symmetry. They are found in the silver-mining districts of Mexico, Colorado, Nevada, &c., sometimes in sufficient abundance to be of importance as ores of silver. **L. J. S.**

POLYCHREST SALT. An old name for normal potassium sulphate; applied also sometimes to Rochelle salt.

POLYCHROMINE r. Primuline and its Derivatives.

POLYGALIC ACID r. Senega.

POLYGONIN r. Glucosides.

POLYGONUM CUSPIDATUM. *P. cuspidatum* (Sieb. et Zucc.), is common in India, China, and Japan, and is referred to by A. Henry in a paper entitled 'Chinese Names of Plants ' (Journal Royal China Branch of Royal Asiatic Society, 22, New Series, No. 5, 1887) as ' Kan-yen, wu-tzu.' the name at Patung for the root of the P. cuspidatum, which is said to be used for dyeing yellow.

According to Perkin (Chem. Soc. Trans. 1895, 67, 1084), the main constituent of this root is a glucoside *polygonin* $C_{21}H_{20}O_{10}$, forming orange-yellow needles. m.p. 202°-203°, which, when hydrolysed by acids, gives *emodin* and a sugar.

$$C_{21}H_{20}O_{10} + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6$$

A trace of a second glucoside is also present, from which the *emodin monomethylether*, m.p. 200°, previously found to exist in the root bark of the *Ventilago madraspatana* (Gaertn.) (Chem. Soc. Trans. 1894, 65, 932) was obtained. **A. G. P.**

POLYHALITE. A triple sulphate, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, occurring in some abundance in salt deposits. In the potash-salt beds of Stassfurt in Prussia and Stebnik in Galicia it is more closely associated with rock-salt, anhydrite, and gypsum; and it is also found with these minerals in the salt

salts, as well as the methods of manufacture pursued here.[1]

The village of Stassfurt is situated on the river Bode, not far from Magdeburg, in Prussian Saxony, close to the borders of the small principality of Anhalt. In 1850 Stassfurt numbered 3000 inhabitants; in 1885, owing to the development of the carnallite industry, 16,000, and the adjoining newly-formed village of Leopoldshall (in Anhalt), 4000 inhabitants. The Stassfurt brine-springs are mentioned as far back as 1227, and in the last century 7,000 tons of salt per annum were made there in 30 salt-pans; but about 1815 the production of salt from brine was stopped there, having ceased to be remunerative

in the face of competing brine-springs. In 1839 the Prussian mining office commenced boring for rock-salt, and in 1843 the salt was struck at a depth of 850 feet. The boring was continued for another 1080 feet without getting to the bottom of the stratum of salt; but the brine pumped up was extremely impure, containing, together with sodium chloride, a large quantity of magnesium chloride, potassium chloride, and magnesium sulphate. It was, however, conjectured at once that these salts might be deposited in separate strata, and it was resolved to sink two shafts. These were commenced in 1852, and within five years they had reached a thick stratum of pure rock-salt, after having

FIG. 1.

penetrated a number of strata of other salts, of an aggregate thickness of 530 feet, which were called ' abraumsalze,' because they were at first considered useless, and had to be taken away before getting to the rock salt.

Later on it was found that the salt deposits occupy an enormous basin in the North German Plain, which has been successfully tapped in several other places, of which we mention only Sperenberg, near Berlin, where the boring was continued through the enormous thickness of 3940 feet of salt without getting to the bottom; also at Segeberg, near Lübeck, and in other places. But *potassium* salts in great quantity

until quite recently had been found only in one locality, in the vicinity of Stassfurt, where the ' Abraumsalze ' occur in the Upper New Red Sandstone. According to Chem. Zeit., Aug. 22, 1911, large deposits of sylvine have been discovered in Upper Alsace, in an area of about 200 square kilos., near Mülhausen. Two strata have been found, the upper one 3 feet thick, the lower one more than 16 feet thick estimated to contain some 1500 tons, but the borings will have to be deep, say 1600 to 2100 feet, which entails a very high temperature. This field, unlike the North German deposits, seems to be continuous, without faults. Geologically it is much more recent than the Stassfurt beds. But the recovery of potassium salts from the Alsatian field has not yet become a commercial fact, and we therefore confine our description to the Stassfurt deposit :—

In 1856 and 1857, the two Prussian shafts at Stassfurt ; in 1861, the Anhalt shaft at Leopoldshall ; in 1876, two shafts at Douglashall, near Westeregeln ; in 1876, a shaft at Neu-Stassfurt ; in 1878–1883, another two shafts at Stassfurt;

[1] In this part we follow to a great extent the detailed description by Pfeiffer, in his Handbuch der Kali-Industrie, Braunschweig, 1887 (cf. also, for some details, Hake, J. Soc. Chem. Ind. 1883, 146 ; and Borsche, J. Soc. Chem. Ind. 1888, 296 ; Kubierschky, Die Deutsche Kaliindustrie (1908), Krische, Die Verwertung des Kalis (1909) ; Ehrhardt, die Kaliindustrie (1907) ; Precht, die norddeutsche Kaliindustrie (1907)). A very important series of researches on the formation of the Stassfurt deposits has been made by van 't Hoff and his coadjutors, in 1897 and later on.

in 1883, a shaft at Aschersleben, sunk by the Continental Diamond Rock-Boring Company; some more shafts at Solvay's mines, near Bernburg, at Schönebeck, &c.; the Hercynia shaft at Vienenburg.

The profiles (Figs. 1 and 2) give an idea of the strata pierced in the two oldest and most important shafts at Stassfurt and Leopoldshall.

At Stassfurt itself the total thickness of the salt strata is estimated at about 2500 feet, and the time necessary for their formation at about 8000 years. F. Bischof, who has examined them most thoroughly, divides them into the four following 'regions,' of which only the first and the last have become of technical importance.

1. *Anhydrite or rock-salt region*, so called from the strings of anhydrous calcium sulphate which divide the rock-salt into bands of an average thickness of nearly 4 inches, each of which is supposed to be a year's growth. The layers of calcium sulphate are only $\frac{1}{4}$ inch thick, and amount only to 4 p.c. by weight of the rock-salt in the upper strata, or 9 p.c. in the lower strata.

Fig. 2.

By mechanically separating the anhydrite, rock-salt of 99 p.c. NaCl can be obtained on a large scale. Small quantities of *hydroboracite*

$$(CaMgB_6O_{11},6H_2O)$$

and of a strontium sulphate are found here as well. The thickness of this stratum varies a great deal: in the centre of the basin it may be estimated at about 2000 feet.

2. *Polyhalite region.* Here the rock-salt is already mixed with mother-liquor salts, of which the dominant one is *polyhalite*

$$2CaSO_4,MgSO_4,K_2SO_4,2H_2O.$$

Magnesium chloride accompanies the rock-salt, and small quantities of sulphur and of bituminous substances are found here. The average composition of this stratum is: 91 rock-salt, $6\frac{1}{4}$ polyhalite, $\frac{3}{8}$ anhydrite, $1\frac{1}{4}$ magnesium chloride; its thickness is 207 feet.

3. *Kieserite region*, so called from the occurrence of white bands of kieserite $MgSO_4,H_2O$. The average mixture is:

65 p.c. rock-salt
17 „ kieserite
13 „ carnallite
3 „ bischofite, $MgCl_2,6H_2O$
2 „ anhydrite.

This stratum has a thickness of 187 feet.

4. *Carnallite region.* This contains 55 p.c. of *carnallite* $KCl,MgCl_2,6H_2O$, the most valuable of the Stassfurt salts, together with 25 p.c. rock-salt, 16 p.c. kieserite, the remaining 4 p.c. consisting of magnesium chloride (*bischofite*) $MgCl_2,6H_2O$, magnesium bromide $MgBr_2,6H_2O$, tachydrite $(CaCl_2,2MgCl_2,12H_2O)$, boracite or stassfurtite $(2Mg_3B_8O_{15})$, anhydrite $CaSO_4$, reichhardtite $(MgSO_4,7H_2O)$, clay, sand, micaceous oxide of iron, &c. The thickness of this stratum is 140 feet.

place through the oxygen atoms, and meta-propaldehyde and parapropaldehyde are probably examples of *cis-trans* isomerism (Orndorff and Balcom, *l.c.*).

PROPCESIN; PROPONAL *v.* SYNTHETIC DRUGS.

PROPIOLIC COMPOUNDS. From propiolic acid, HC: C·COOH, may be derived a series of acids of the general formula C_nH_{2n+1}·C:C·COOH, and the members of this series may be regarded as the true homologues of propiolic acid, although the isomeric acids, in which the acetylene linkage is not in the α-β position, are often also described as propiolic compounds. The alkyl group may be replaced by an aromatic radicle, *e.g.* in phenyl propiolic acid C_6H_5·C:C·COOH, the nitro-derivative of which is important as being the initial substance in Baeyer's original synthesis of indigo.

Alkylpropiolic acids R·C:C·COOH. Methods of formation:

1. By the action of carbon dioxide on the sodium acetylenes—

R·C:CNa+CO_2=R·C:C·COONa.

A convenient modification of this synthesis is to employ chlorocarbonic ester and saponify the product—

R·C:C·Na+Cl·$COOC_2H_5$=NaCl+R·C:C·$COOC_2H_5$
(Moreu and Delange, Compt. rend. 1903, 136, 552).

2. By the action of dilute aqueous potash on the chloro derivatives of the acrylic acids—

R·CCl:CH·COOH−HCl=R·C:C·COOH.

Reactions.—1. On reduction with sodium amalgam the corresponding fatty acid is obtained.

2. On boiling with alcoholic potash β-ketonic acids are formed—

R·C:C·COOH+H_2O=R·CO·CH_2·COOH
(Moreu and Delange, Compt. rend. 1902, 136, 733).

3. On heating with aqueous potash a ketone is obtained—

R·C:C·COOH+H_2O=R·CO·CH_3+CO_2.

4. The propiolic esters react readily with alcohols and amines, forming addition compounds, and also with hydrazine forming pyrazole derivatives (Moreu and Lazennec, Compt. rend. 1906, 143, 596, and 1239).

Propiolic acid, propargylic acid,

H·C:C·COOH,

was discovered by Bandrowski, who obtained it by warming the aqueous solution of the acid potassium salt of acetylene dicarboxylic acid. It is a colourless liquid, slightly heavier than water, with a strong smell of acetic acid, freely soluble in water and organic solvents, m.p. 9°, b.p. 140°-145° (decomposition). Propiolic acid is a stronger acid than acetic acid, which is attributed to the negative nature of the acety-lene linkage. Its alkali and alkaline earth salts are characterised by excessive solubility in water; on boiling their solutions there is gradual decomposition

2HC:C·COOK=K_2CO_3+CO_2+$2C_2H_2$.

Owing to the fact that there is an acetylene hydrogen atom present, propiolic acid, its salts and esters are capable of forming characteristic metallic derivatives, such as

AgC:C·$COOC_2H_5$, CuC:C·COONa, &c.

The copper compound on oxidation with potassium ferricyanide yields a propiolic deriva-tive containing two acetylene linkages

(·C:C·COOH)$_2$

and by the elimination of a carboxyl group and the subsequent oxidation of the copper compound of the substance thus obtained, Baeyer was able to perform a synthesis of the acid (·C:C·C:C·COOH)$_2$, containing four acetylene linkages (Ber. 1885, 18, 2269).

Propiolic aldehyde HC:C·CHO has been obtained by Claison (Ber. 1898, 31, 1022; 1903, 36, 3664) from the acetal of dibromo-acrolein by converting it into propiolic acetal by the action of potash and then eliminating the ethoxyl group by means of dilute sulphuric acid. It is a colourless mobile liquid, b.p. 60°, with an even more pungent odour than acrolein. Like propiolic acid, it forms silver and copper deriva-tives. The aldehyde group is attached to the acetylene nucleus even less firmly than the carboxyl in propiolic acid, cold aqueous alkalis causing immediate decomposition—

HC:C·CHO+KOH=C_2H_2+H·COOK.

Similarly hydroxylamine and phenylhydrazine do not condense normally, but yield cyclic products, namely isoxazole and pyrazole.

Methylpropiolic acid CH_3·C:C·COOH, m.p. 76°, b.p. 203°. The esters of this acid and the higher homologues find some application in the preparation of artificial perfumes (Moreu, D. R. PP. 133631; 158252).

Phenylpropiolic acid C_6H_5·C:C·COOH, has been obtained by the action of sodium and carbon dioxide on bromophenylacetylene, C_6H_5·C:CBr; by the action of carbon dioxide on sodium phenylacetylene C_6H_5·C:CNa; by the action of alcoholic potash on bromocinnamic acid or on phenyldibromopropionic acid. White crystals slightly soluble in water, m.p. 137°; it forms soluble salts, the sodium salt having strong disinfecting properties (Kozai, Chem. Zentr. 1906, i. 1758). Reactions: On heating it loses carbon dioxide and forms phenylacetylene; chromic anhydride oxidises it to benzoic acid; on reduction with zinc dust and acetic acid cinnamic acid is formed; bromine is added readily with the production of two isomeric dibromo-cinnamic acids; acetic anhydride causes condensation to a phenylnaphthalene derivative (Bucher, J. Amer. Chem. Soc. 1910, 32, 212).

o-**Nitrophenylpropiolic acid**

$C_6H_4(NO_2)$·C:C·COOH

(*see* INDIGO, ARTIFICIAL) was first obtained by Baeyer, who utilised it in the synthesis of indigo. On nitrating cinnamic acid the ortho-derivative is obtained; if this is converted into the dibromo acid by the addition of bromine and the product treated with alkali, *o*-nitrophenylpropiolic acid results (Baeyer, Ber. 1880, 13, 2258; D. R. P. 11857). On reduction in alkaline solution, it gives first isatogenic acid, and then loses carbon dioxide to form indigo; or by heating it may be converted by loss of carbon dioxide into *o*-nitrophenylacetylene, the copper compound of which may be oxidised by potassium ferricyanide to the diacetylene derivative, and this on re-duction yields indigo. On treating with alkalis *o*-nitrophenylpropiolic acid forms isatin; by the action of concentrated sulphuric acid, isatogenic acid (Baeyer, D. R. P. 17050).

Name	Origin	Class
Phycocyan,[1] Phycoerythrin	Ceramium rubrum	Chromoproteins
Ricin	Castor bean	Albumin
Tuberin	Potato tuber	Globulin
Vicillin	Lentil, horse-bean, vetch, etc.	Globulin, precipitated by $\frac{7}{10}$ saturation with ammonium sulphate.
Vignin	Cow-pea	Globulin
Zein	Maize	Prolamine

Animal Proteins.

Name	Origin	Class
Albumin of egg (ovalbumin)	Eggs	Albumin
Albumin of milk (lact-albumin)	Milk	,,
Albumin of serum	Serum	,,
Bence-Jones protein	Certain pathological urines	Globulin (?)
Caseinogen	Milk	Phosphoprotein
Chondroproteins	Cartilage, tendons, etc.	Glycoproteins
Clupeine	Testes of herring	Protamine
Collagen	Connective tissue	Scleroprotein
Conalbumin (?)	Eggs	Albumin
Conchiolin	Shell of lamellibranchs	Scleroprotein
Cornein	Coral	Scleroprotein
a- and β-Crystallins	Lens of eye	Globulins
Cyclopterine	Testes of cyclops	Protamine
Elastin	Ligamentum nucæ	Scleroprotein
Fibrinogen. Yields fibrin on clotting	Blood	Globulin.
Gadus histone	Testes of Gadus	Histone
Gelatin	Closely allied to collagen	Scleroprotein
Globin	Separated from chromo-protein of blood.	Histone (?)
Globulin of egg (ovoglobulin)	Eggs	Globulin
,, milk (lacto-globulin)	Milk	,,
,, serum	Serum	,,
Gorgonin	Skeletal tissue, Gorgonia cavollini	Scleroprotein.
Hæmoglobin	Blood	Conjugated protein
Histone of thymus	Thymus gland	Histone
Keratins (various)	Hair, horn, nails, etc.	Scleroproteins
Lota histone	Testes of Lota	Histone
Myosin (para myosinogen)	Striated muscular tissue	Globulin
Myogen (myosinogen)	,, ,, ,,	Albumin
Mucins and mucoids	Various secreting glands (Animal mucilagenous substances generally)	Glycoproteins
Nucleoproteins	Animal and vegetable cells (supposed constituent of nucleus)	Nucleoproteins
Onuphin	Onuphis tubicola (worm)	Scleroprotein
Reticulin	Mucosa, small intestine of pig, etc.	,,
Salmine	Testes of salmon	Protamine
Scombrine	Testes of mackerel	,,
Silk gelatin	Silk	Scleroprotein
Silk fibroin	Silk	,,
Spongin	Sponges	,,
Sturine	Testes of sturgeon	Protamine
Thyreoglobulin	Thyroid gland	Globulin
Vitellin	Yolk of eggs	Phosphoprotein

IV. The Separation and Identification of the Natural Proteins.

One of the chief difficulties encountered in the investigation of the proteins is that due to their separation from one another. So great has this been that in very many of the cases it is impossible to state whether a substance described under a given name is a chemical entity or a mixture. In the case of insoluble substances, such as the keratins, this statement can be readily understood. But even in the case of the soluble proteins, no satisfactory method for complete separation exists. This is due to the colloidal nature of the substances, so that if one substance is separated from solution, it will carry down with it, in state of adsorption, other substances, which in its absence would remain in solution. For these

[1] Kylin, Zeitsch. physiol. Chem. 1910, 69, 169.

closely allied. The reaction is characteristic rather of the species of the animal from which the antigen is derived than of its actual chemical characteristics. Thus a precipitin-yielding serum obtained by the injection of human blood into rabbits will give a precipitation with any of the proteins derived from the human body, and if the rabbit had been properly ' immunised ' with a sufficient number of injections it will precipitate these proteins in very dilute solutions. Proteins derived from a species zoologically allied to a man, such as anthropoid apes, it will precipitate, but only in more concentrated solutions than are necessary to produce a precipitate in the case of proteins of human origin. This ' precipitin ' reaction has been employed practically in meat inspection to determine the origin of the meat in sausages and other meat-containing material, when the origin cannot be ascertained by direct inspection. As to the chemical or physical nature of the precipitin reaction little is known.

V. The Conjugated Proteins.

(a) The Nucleoproteins.

This important class of proteins is found in most tissues, the nucleoproteins being generally assumed to be the chief constituent of the cell nucleus. They were first systematically investigated by Miescher, who showed that the spermatozoa of salmon and various other fish were composed chiefly of compounds of the strongly basic protamines, with an amorphous acid called nucleic acid. Nucleic acid is the essential non-protein group in this class of conjugated proteins, and is found in combination with other proteins than the strongly basic protamines. The nucleo-proteins can be extracted from tissues, &c., by dilute salt solutions or very dilute alkali. From the solution thus obtained they can be precipitated by dilute acetic acid. It is sometimes advisable to dry the tissues before extracting by treating with gradually increasing concentrations of alcohol, and finally with absolute alcohol and ether. On digesting nucleoproteins with enzymes, the protein part of the molecule is partially hydrolysed and a residue, soluble in alkalis, but insoluble in dilute acetic acid, is obtained, which is termed a nuclein.

Nucleic acid. It is important in this article to give a short account of this acid, which, although not a protein, is found only in combination with proteins to form substances of great physiological importance. As to the number of nucleic acids and the identity of the nucleic acids from various sources, nothing quite definite can be stated at the present time, although Steudel affirms that the nucleic acid obtained from such different sources as fish-spermatozoa and thymus gland of calf are identical.

Nucleic acid was originally obtained by Miescher by treating the nucleoprotein from fish spermatozoa with sodium hydroxide solution and throwing the solution of sodium nucleate thus obtained into an ice-cold solution of hydrochloric acid in alcohol. The operations must be carried out rapidly, as the nucleic acid is readily decomposed by mineral acids. The acid is, however, more stable in the presence of alkalis,

and is now generally prepared directly from tissues, &c., without previously isolating the nucleoprotein. Thymus gland gives the largest yield. The gland is boiled with alkali, the hydrolysis mixture, after solution of the proteins, neutralised with acetic acid, and the filtrate from the precipitate thus obtained, thrown into alcohol, whereby sodium nucleate is precipitated ; this is purified by solution in water and reprecipitation by alcohol. The free acid can be obtained from the sodium salt by alcoholic hydrochloric acid. Nucleic acid is a strong acid, which gives soluble alkali salts from solutions of which the free acid can be precipitated by mineral acids, but not by acetic acid. A 5 p.c. solution of sodium nucleate forms a gel. On hydrolysis with acids it yields the following groups of substances: (a)alloxuric bases(guanine, adenine, xanthine, and hypoxanthine ; (b) pyrimidine bases, cytosine, uracil, and thymine ; (c) carbohydrate derivatives, formic and lævulic acids, decomposition products of hexose ; (d) phosphoric acid and ammonia. Of these products, xanthine, according to Steudel, is a secondary decomposition product produced by the action of acids on guanine, with scission of ammonia, and hypoxanthine and uracil are in a similar way produced from adenine and cytosine respectively. Steudel represents the hydrolysis of nucleic acid as follows :

$$C_{43}H_{57}N_{15}O_{30}P_4 + 8H_2O + 2O = C_5H_5N_5O + C_5H_5N_5$$
$$\text{(Guanine)} \qquad \text{(Adenine)}$$
$$+ C_5H_6N_2O_2 + C_4H_5N_3O + 4C_6H_{12}O_6 + 4HPO_3$$
$$\text{(Thymine)} \quad \text{(Cytosine)} \quad \text{(Hexose).}$$

According to this scheme, nucleic acid is a tetra-metaphosphoric acid, containing for each atom of phosphorus a hexose group (compare the glycerophosphates) and one molecule of a base. Recent researches of Levene and his pupils indicate that the ordinary nucleic acid is formed by the coupling up of single groups, termed nucleotides, each of which consists of a phosphoric acid residue combined with a carbohydrate and a base. The nucleic acid of thymus would be formed from four such groups, each containing a different base. The nucleotides themselves can be broken down, according to the method of hydrolysis, into complexes containing phosphoric acid and a carbohydrate, or into complexes containing carbohydrate and base (Ber. 1908, 41, 1905, 2703 ; 1909, 42, 335, 1198, 2474, 2469, 2703).

Nucleic acids from yeast, wheat embryos, and other sources have also been investigated. Certain other allied substances, such as guanylic acid (from pancreas) and inosinic acid (from meat extract) have been described, which yield on hydrolysis pentoses instead of hexoses. These are possibly nucleotides (see papers of Levene already quoted above).

b. The Glycoproteins.

In this group is included a large number of mucilaginous substances, which are widely distributed in the animal kingdom. Included amongst them are the mucins of egg-white serum, salivary glands, ascitic fluids, &c. They are, for the most part, precipitated from solutions by very weak alkali. Properly speaking, they should not perhaps be classed as conjugated

is formed. By this treatment it loses a molecule of water, forming an anhydride, *quasside*, $C_{2}H_{30}O_{7}$. This compound, which is white, amorphous, and bitter, melts at $192°-194°$ and when boiled with dilute alcohol, takes up again a molecule of water, quassin being re-formed. Quassin may also be converted into the anhydride by heating with acetic anhydride, or even by heat alone at $150°$ in a current of dry air. If bromine be present *tribromoquassiae*, $C_{32}H_2Br_3O_9$, results. If quassin be heated with acetic anhydride in presence of sodium acetate the dehydration goes further. In this case two molecules of water are removed, and a *second anhydride*, $C_{32}H_{32}O_9$, a white, pearl-like, amorphous mass, melting at $150°-158°$, is obtained. Bromine forms with quassin a substitution derivative melting at $155°$, *bromoquassin*, $C_{32}H_4Br_3O_9$ (?), and phosphorus pentachloride yields *penta-chloroquassin*, $C_{32}H_{30}Cl_5O_9$ (?), a yellow powder melting at $119°$. A *nitro* derivative melting at $130°$ also exists (D. and O.). When quassin is heated with concentrated hydriodic acid and amorphous phosphorus it yields, among other products, *isodurene*, $C_{10}H_{14}$, and a *hydrocarbon*, $C_{16}H_{16}$, which boils at $230°-240°$ (Oliveri, Gazz. chim. ital. 17, 575).

From the investigations of Massute (Arch. Pharm. [iii.] 28, 147) it would appear that the bitter crystalline constituents of the different trees mentioned at the beginning of this article, although similar, are not identical. By an improved process this observer obtains from the wood of *Q. amara* four bitter crystalline *quassins*, one of which corresponds with the quassin of Oliveri and Denaro. The others are probably methyl derivatives of this with higher melting-points. From *P. excelsa* the same chemist obtains two crystalline compounds which are designated *picraemine*. They differ in composition from the *quassins*, but appear also to be methyl derivatives or homologues. One of them yields, by the action of hydrochloric acid, *picraemic acid*, homologous with the quassic acid of Oliveri and Denaro. By extracting crude quassin with ether, Merck (Chem. Zentr. 1895, i. 435) obtained *quassole* $C_{40}H_{70}O+H_2O$ (?) which crystallises in colourless plates melting at $149°-151°$. It differs from quassin by its absence of taste.

Quassia is sometimes used as a substitute for hops in beer. For methods of its detection see Dragendorff (Chem. Zentr. 1881, 285 and 299), Allen (Analyst. 1887, 107), Chapman (*ibid.* 1900, 35). A. S.

QUASSIC ACID, QUASSIDE, QUASSIN, *v.* QUASSIA.

QUEBRACHO COLORADO. The quebracho colorado are anacardiaceous trees belonging to the genus *Quebrachia*, growing in the northern part of the Argentine Republic, the wood of which constitutes the well-known tannin substance ‘quebracho.’ It is imported into this country in the form of logs and is employed for tanning, either in the chipped condition or in the form of extract. Their wood is extremely hard, as the name ‘quebracho’ (axe-breaker) denotes, and its sp.gr. varies from 1·27 to 1·38.

Jean (Bull. Soc. chim. 1890, 33, 6) found that it contained 15·7 p.c. of a tannic acid not identical with that of oak bark or chestnut wood, whereas Procter (Leather Manufacture,

1903, 269) estimates it to contain about $3°$ p.c. of a tannin yielding reds .phlobophane. and containing catechol and phlorogluctnol nuclei. This tannin is somewhat sparingly soluble in water and can only be used in weak liquors, but gives a firm reddish leather.

In order to isolate the tannin, Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 19, 1121) extract the bark first with chloroform and then with alcohol. Addition of water to the alcoholic extract causes the separation of phlobophanes, and from the clear liquid concentrated in a vacuum the tannin is precipitated by lead acetate, the lead salt being collected suspended in water and decomposed with sulphuretted hydrogen. The resulting solution is evaporated to dryness, the residue dissolved in alcohol and poured into ether. Thus obtained it consists of a light flaky mass, which is hygroscopic and becomes sticky on exposure to moist air.

According to Arata (J. 1879, 306), *quebracho tannin* $C_{26}H_{24}O_{10}$, gives *catechol* on dry distillation, with nitric acid *oxalic* and *picric acids*, by fusion with alkali *phloroglucinol* and *protocatechuic acid*, whereas, by the latter method, Nierenstein isolated also *hydroquinone* and *resorcinol* (Collegium. 1905, 65). According to the latter author, the quebracho colorado probably contains three tannins. By treating a cold aqueous extract of the quebracho colorado with bromine, Böttinger (Ber. 17, 1123) obtained a reddish-yellow compound containing 42·1 to 44·5 p.c. of bromine. Nierenstein, who isolated the tannin according to Trimble's method (The Tannins), treated the solution with lead acetate, filtered, and on adding bromine to the clear liquid obtained a precipitate of *monobromoque-brachotannin* $C_{16}H_{14}Br_2O_5$. which consists of a cinnabar red powder, and on digestion with alcoholic potash gives iso*vanillic acid* and *monobromoquebrachylic acid* needles, m.p. $119°-120°$.

Strauss and Geschwender (*l.c.*) consider that quebracho tannin is identical with maletto-tannin, and with the tannin from cinchona bark, and ascribe to it the formula $C_{42}H_{36}O_{20}$. With a mixture of acetic anhydride and acetic acid the *acetyl* compound $(C_{36}H_{22}O_{11}Ac_6)_2$, colourless powder, is produced, and a corresponding *benzoyl* derivative $(C_{36}H_{22}O_{11}Bz_6)_2$ can also be prepared.

Quebracho phlobophane, on distillation with zinc dust, yields anthracene (Nierenstein, Ber. 1907, 40, 4575).

According to Arnaudon the wood contains a colouring matter which gives a fine yellow dye, and this has been examined by Perkin and Gunnell (Chem. Soc. Trans. 1896, 69, 1304) and found to be identical with *fisetin*, the colouring matter of young fustic. This compound, which appears to exist in the wood as glucoside, gives on fusion with alkali protocatechuic acid and resorcinol, and may account for the appearance of the latter phenol among the hydrolytic products of the crude tannin itself. According to Perkin and Gunnell, when an extract of the quebracho colorado is digested with boiling dilute acid a small quantity of *ellagic acid* is obtained.

In addition to the tannins above described, the quebracho colorado is the source of the so-called ‘quebracho resin,’ which collects as a thickened juice in the crevices of the tree. It has been examined by Arata (Chem. Soc. Abstr.
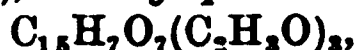
still present in this compound, and it yields with alcoholic potash a bright yellow salt decomposable by water, and a *monoacetyl* derivative $C_{15}H_5O_2(C_2H_3O)(OCH_3)_4$, needles, m.p. 167°–169° (H.). The *ethylation* product
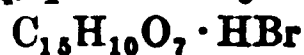
$$C_{15}H_6O_2(OC_2H_5)_4$$

yellow needles, m.p. 120°–122°, is similarly constituted, and gives the *acetyl* compound $C_{15}H_5O_2(OC_2H_5)_4(C_2H_3O)$, m.p. 151°–153°.

When heated with alcoholic potash, quercetin tetramethyl ether forms *veratric acid* and a syrupy phloroglucinol derivative (H.), and this latter has been shown (Perkin and Allison, Chem. Soc. Trans. 1902, 81, 471) by means of its disazobenzene derivative to consist of *phloroglucinol monomethyl ether.* Quercetin tetraethyl ether exhibits a similar behaviour.

The following is a list of the more important derivatives of quercetin : *Dibromquercetin* $C_{15}H_8Br_2O_7$, yellow needles, m.p. 233°–235° (H.), *acetyl dibromquercetin* $C_{15}H_7Br_2O_7(C_2H_3O)_5$ (H.), *dibromquercetin tetraethyl ether*, yellow needles, m.p. 169°–173°, *quercetin triphenylcarbamide* $(OH)_2 \cdot C_{15}H_5O_5(OCO \cdot NH \cdot C_6H_5)_3$ (Tesmer, Ber. 1885, 18, 2609), *triacetyl quercetin*

$$C_{15}H_7O_7(C_2H_3O)_3,$$

colourless needles, m.p. 167°–169°, and *tetra-acetyl quercetin* $C_{15}H_6O_7(C_2H_3O)_4$, m.p. 193°–194° (Perkin, Chem. Soc. Trans. 1899, 75, 449), *benzoyl quercetin* $C_{15}H_5O_7(C_7H_5O)_5$, m.p. 239° (Dunstan and Henry, Chem. Soc. Trans. 1898, 73, 219). With mineral acids in the presence of acetic acid, quercetin gives *quercetin sulphate* $C_{15}H_{10}O_7 \cdot H_2SO_4$, *quercetin hydrobromide*

$$C_{15}H_{10}O_7 \cdot HBr$$

quercetin hydrochloride $C_{15}H_{10}O_7 \cdot HCl$, and *quercetin hydriodide* $C_{15}H_{10}O_7 \cdot HI$, which crystallise in orange needles and are decomposed by cold water (P. and P.). *Monopotassium quercetin* $C_{15}H_9O_7K$ and *monosodium quercetin* $C_{15}H_9O_7Na$, orange needles, are produced by the action of alcoholic potassium and sodium acetates (Perkin, Chem. Soc. Trans. 1899. 75, 438). *Aminoquercetin* $C_{15}H_4O_5(OH)_5NH_2$, pale yellow needles, has been obtained by Watson (Proc. Chem. Soc. 1911, 27, 163) by the action of hydriodic acid (1·7) on aminopentamethyl-quercetin. The *hydrochloride* $C_{15}H_{11}O_7 \cdot N \cdot HCl$, yellow needles, the *hydriodide*, *sulphate*, and *acetyl* derivative, colourless rhombs, m.p. 151°–153°, are also described. Aminoquercetin dyes mordanted wool browner and deeper colours than quercetin itself.

Quercetin is a strong dyestuff, and gives with mordanted wool the following shades, which are almost indentical with those produced by fisetin :—

Chromium	Aluminium	Tin	Iron
Red-brown	Brown-orange	Bright orange	Olive-black

The suggestion that quercetin was probably *hydroxyfisetin* is due in the first place to Herzig, and this has been substantiated by the synthesis of this colouring matter (*see* below).

It has been found (Waliaschko, Arch. Pharm. 1904, 242, 225) that by employing methyl sulphate in the methylation of quercetin, *quercetin pentamethyl ether* $C_{15}H_5O_2(OCH_3)_5$, colourless needles, m.p. 148°, can be produced.

From quercetin pentamethyl ether Watson (Proc. Chem. Soc. 1911, 27, 163) has prepared

the following compounds : *Nitropentamethyl-quercetin* $C_{15}H_4O_2(OCH_3)_5 \cdot NO_2$, yellow needles, m.p. 202°–204°, *aminopentamethylquercetin* $C_{15}H_4O_2(OCH_3)_5 \cdot NH_2$, colourless prisms, m.p. 200°–202°, *pentamethylquercetin hydrobromide* $C_{20}H_{20}O_7 \cdot HBr$, *hydrochloride* $C_{20}H_{20}O_7 \cdot HCl$, *sulphate* $C_{20}H_{20}O_7 \cdot H_2SO_4$, *nitrate*

$$C_{20}H_{20}O_7 \cdot HNO_3,$$

yellow needles, *trinitropentamethylquercetin* $C_{15}H_2O_2(OCH_3)_5(NO_2)_3$, m.p. 190°–205°, *dibrompentamethylquercetin* $C_{15}H_3O_2 \cdot Br_2 \cdot (OCH_3)_5$, colourless prisms, m.p. 173°–175°, *dibrompentamethylquercetin hydrobromide* $C_{20}H_{18}O_7 \cdot Br_2 \cdot HBr$, *dibromnitropentamethylquercetin*

$$C_{15}H_2O_2Br_2 \cdot (OCH_3)_5NO_2,$$

yellow rhombs, m.p. 173°–175°, *pentamethylquercetin diazonium chloride*

$$C_{15}H_4O_2 \cdot (OCH_3)_5 \cdot N_2 \cdot Cl,$$

yellow needles, *sulphate* yellow needles, and *pentamethylquercetin-azo-β-napthol*

$$C_{15}H_4O_2(OCH_3)_5 \cdot N_2 \cdot C_{10}H_6OH.$$

Pentamethylquercetin, when hydrolysed with alcoholic potash (Herzig, Ber. 1909, 42, 155). gives, together with *veratric acid,* the *methoxy derivative of the fisetol dimethyl ether,* which he obtained (Monatsh. 1891, 12, 187) by the hydrolysis of fisetin tetramethyl ether. The reaction may be expressed as follows :—

Quercetin pentamethyl ether.

Intermediate compound.

Hydroxy pentamethoxybenzoylacetophenone.

Methoxy fisetol dimethyl ether.

and affords a clear proof of the flavonol constitution of quercetin—

Quercetin has been synthesised by v. Kostanecki, Lampe, and Tambor (Ber. 1904, 37, 1402) by a series of reactions similar to those which had been successfully employed for the preparation of fisetin. The starting-point of

synthetical method may afford the information required. For derivatives containing the substituent in the 'benzene' ring, Skraup's synthetical method is invaluable, as the interpretation of the results is free from ambiguity except in the case of syntheses from *meta*-substituted anilines, which may give rise to both *meta*- and *ana*- derivatives of quinoline. Methods for meeting this difficulty have been devised by Skraup and Brunner (Monatsh. 1886, 7, 139), Tortelli (Gazz. chim. ital. 1886, 16, 336), and Lellmann and Alt (Annalen, 1887, 237, 315).

Comparison of the properties of quinoline and naphthalene.—In quinoline, which differs structurally from naphthalene by containing a tervalent nitrogen atom in place of one of the *a*-methenyl groups, certain of the characteristics of this hydrocarbon are reproduced. Thus, 5-aminoquinoline-4-carboxylic acid yields an internal anhydride (Koenigs and Lossow, Ber. 1899, 32, 717); and lakes are formed by 8-hydroxyquinolines but not by their isomerides (Noelting and Trautmann, ibid. 1890, 23, 3660). But the presence of a nitrogen atom in one of the rings destroys the symmetry of the molecule; consequently the number of mono-substitution derivatives becomes seven instead of only two as in naphthalene. Moreover, reactivity, associated in naphthalene with the *a*- (1-, 4-, 5-, or 8-) position is restricted in quinoline, as in pyridine, to the 2- and 4- positions (cf. *inter alia*, Koenigs, Ber. 1901, 34, 4326; Ephraim, ibid. 1891, 24, 2818; 1892, 25, 2706; 1893, 26, 2227; Henrich, ibid. 1899, 32, 674), and to these in an approximately equal degree (cf. however, Koenigs and Mengel, ibid. 1904, 37, 1323).[1]

The orientating effect of the cyclic nitrogen atom in quinoline resembles closely that of the nitro- group in *a*-nitronaphthalene. For example, each directs the NO_2 or the SO_3H group into both the 5- and the 8- position, this being true also not only of quinoline, but of its derivatives so long as strongly 'positive' (e.g. OH or NH_2), or strongly 'negative' (e.g. NO_2 or SO_3H) radicles, which themselves exercise a directing influence, are absent from the molecule (Decker and Kaufmann, J. pr. Chem. 1911, [2] 84, 238; Decker and Remfry, Ber. 1905, 38, 2774).

Uses of Quinoline Derivatives.

Quinoline derivatives, in addition to their limited use in the manufacture of dye-stuffs (v. *Cyanines*, p. 481), have found employment as antipyretics and antiseptics. Quinoline and 6-methoxyquinoline are decomposition products of cinchonine and quinine respectively; investigation of the antipyretic properties of these products showed, however, that the specific action which renders quinine so valuable in cases of malaria is not possessed by them (cf. Stockmann, J. Physiol. 1894, 15, 245; Fühner, Arch. exp. Path. Pharm. 1905, 55, 27); also that 6-methoxyquinoline, which might be expected to excel quinoline in this respect, is the weaker antipyretic of the two (Jaksch, Prager med. Wochensch. 1881, No. 28).

McKendrick and Dewar having shown that

[1] Susceptibility of the methylquinolines to oxidation by chromic acid does not follow this rule but diminishes in the order 5, 6, 7, 8, 4, 3, 2, the methyl group in the 5-position being the most and that in the 2-position being the least reactive (Miller, Ber. 1890, 23, 1256).

reduction (hydrogenation) intensified the physiological effect of bases of the pyridine and quinoline series (Roy. Soc. Proc. 1874, 22, 290), the physiological action of the tetrahydroquinolines was examined, but the results did not fulfil expectation. The best known of these reduction products, kairoline, thalline, and kairine:

Kairoline. Thalline. Kairine.

have marked antipyretic properties—those containing a methyl group in the 1-position being the more valuable (Filehne, quoted, Ber. 1883, 16, 719, 739)—but they all lack the specific properties of quinine.

The relationship of 4-phenylquinoline to apoquinonine, and therefore to the cinchona alkaloids (Koenigs and Nef, Ber. 1890, 19, 2427; Koenigs, ibid. 1894, 27, 901; Koenigs and Meimberg, ibid. 1895, 28, 1045) led to the investigation of 6-methoxy- and other derivatives of this base (Koenigs and Jaeglé, ibid. 1895, 28, 1046; Meister, Lucius & Brüning, D. R.-P. 79173, 79871, 80501 of 1894), but although certain of them are antipyretics, they are useless against malaria, and give rise to dangerous after-effects (cf. Mannaberg, Deutsch. Arch. klin. Med. 1897, 59, 185).

Another group of derivatives investigated in this connection are the quinoline analogues of phenacetin. Analgen (8-ethoxy-5-acetyl-aminoquinoline) and benzanalgen, the benzoyl-derivative, have antipyretic and antirheumatic properties, which are shared by the 6-ethoxy-derivative, but their insolubility in water and uncertainty in action render them useless in medicine.

Quinoline inhibits putrefaction, but not alcoholic fermentation (Donath, Ber. 1881, 14, 1769). Crurin is the bismuth compound of quinoline thiocyanate, for which antiseptic properties have been claimed (Edinger, D. R.-P. 80768, 86251; Eng. Pat. 18516 of 1894; D. R.-P. 86148 of 1895). As iodoform substitutes, vioform (iodo-5-chloro-8-hydroxyquinoline), loretin (7-iodo-8-hydroxyquinoline-5-sulphonic acid) and other similar compounds have been proposed, but have found no permanent application in surgery.

The following quinophenol derivatives are disinfectants: 'Quinosol,' prepared by heating 8-hydroxyquinoline in alcoholic solution with potassium pyrosulphate, and 'oxyquinaseptol' (diaphtherin) obtained by heating 8-hydroxyquinoline with phenol and diluted sulphuric acid (Lembach and Schleicher, D. R.-P. 73117 of 1892; Eng. Pats. 7803 of 1891; 21968 of 1892).

Synthesis of Quinoline Derivatives.

(i.) *Preparation of derivatives containing radicles substituted in the 'benzene' nucleus.*

Skraup's synthesis. The discovery that not only is quinoline produced by heating aniline with glycerol and sulphuric acid, but that the yield is much increased by the addition of nitrobenzene to the mixture (Skraup, Monatsh. 1880, 1, 317), led to the extension of the method to

as an intermediate product (*cf.* equation (*d*), p. 472)[1]—

$$CH_3 \cdot CHO + Me \cdot CO \cdot R \rightarrow CHMe : CH \cdot CO \cdot R$$
$$C_6H_5 \cdot NH_2 + CHMe : CH \cdot CO \cdot R$$
$$\rightarrow C_6H_4 <^H_{NH \cdot CHMe \cdot CH_2 \cdot CO \cdot R}$$
$$\rightarrow C_6H_4 <^{CR \, : \, CH}_{N \, : \, CHMe} > + H_2 + H_2O.$$

(Beyer, J. pr. Chem. 1885, [2] 31, 48 ; 32, 127 ; 1886, [2] 33, 395).

A similar condensation, with the production of derivatives of quinoline-4-carboxylic (cinchonic) acid, ensues when pyruvic acid, an aldehyde and aniline are warmed together in alcoholic solution (Böttinger, Annalen, 1878, 191, 321 ; Doebner, *ibid.* 1887, 242, 270 ; 1888, 249, 98 ; Pictet and Misner, Ber. 1912, 45, 1801). The course of this reaction may be represented thus (*cf.* equation (*c*), p. 472)—

$$C_6H_5 \cdot NH_2 + R \cdot CHO \rightarrow C_6H_5 \cdot N : CHR + H_2O$$
$$C_6H_5 \cdot N : CHR + CH_3 \cdot CO \cdot CO_2H$$
$$\rightarrow C_6H_4 <^H_{NH \cdot CHR \cdot CH_2 \cdot CO \cdot CO_2H}$$
$$\rightarrow C_6H_4 <^{C(CO_2H) \, : \, CH}_{N \, : \, CR} > + H_2 + H_2O$$

(Simon and Mauguin, Compt. rend. 1907, 144, 1275 ; Borsche, Ber. 1908, 41, 3886).

Process.—To prepare quinoline derivatives by Doebner and Miller's method, aniline or the substituted aniline is mixed with twice its weight of fuming hydrochloric acid, and the requisite quantity of aldehyde added gradually, care being taken to avoid rise of temperature. If a β-hydroxyketone is to be used, the mixture of ketone and aldehyde required for its production must be polymerised by means of hydrogen chloride before it is added gradually to the mixture of aniline and hydrochloric acid. After being heated for many hours on a water-bath, the product is digested with water, the filtrate rendered alkaline by caustic soda solution, the precipitated base freed from secondary amines by treatment in acid solution with nitrite, and the quinoline derivative purified, either by fractional distillation or by conversion into the sparingly soluble crystalline picrate (*cf.* Harz, Ber. 1885, 18, 3384 ; Miller and Kinkelin, *ibid.* 1886, 19, 527 ; Schultz, *ibid.* 1883, 16, 2600 ; 1884, 17, 1965 ; Actieng. für Anilinfab., D. R.-P. 28217 ; Eng. Pat. 4207 of 1883 ; Beyer, J. pr. Chem. 1886, [2] 33, 401 ; Reed, *ibid.* 1887, [2] 35, 299 ; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 35133 of 1885).

(2) **Beyer's synthesis.** In the Doebner and Miller reaction both hydrogen and water are eliminated in the condensation. If a β-diketone is used instead of the β-hydroxyaldehyde or β-hydroxyketone, hydrogen ceases to be one of the products, and the yield of quinoline derivative is improved. To bring about the condensation, the product obtained by heating a mixture of aniline and the diketone in mole-

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· This view of the reaction is supported by the known behaviour of β-anilinoethyl ethyl ketone when heated with aniline hydrochloride

$$C_6H_4 <^H_{NH \cdot CH_2 \cdot CH_2 \cdot CO \cdot Et}$$
$$\rightarrow C_6H_4 <^{CEt \, : \, CH}_{-N \, : \, CH} > + H_2 + H_2O$$

(Blaise and Maire, Bull. Soc. chim. 1908, [4] 3, 667).

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cular proportion is warmed for some hours with concentrated hydrochloric acid :

$$C_6H_5 \cdot NH_2 + Me \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$$
$$\rightarrow C_6H_4 <^H_N : CMe \cdot CH_2 \cdot CO \cdot CH_3 + H_2O$$
$$\rightarrow C_6H_4 <^{C(CH_3) \, : \, CH}_{-N \, : \, CMe} > + H_2O$$

(Beyer, Ber. 1887, 20, 1770 ; Combes, Compt. rend. 1888, 106, 142 ; 1889, 108, 1252).

(3) **Friedlaender's synthesis.** The elimination of hydrogen is avoided also if, instead of aniline and a diketone, a mixture of an *o*-keto-substituted aniline and either an aldehyde or a ketone is used, the condensation proceeding with such readiness that the interacting substances need only be dissolved in water or aqueous alcohol, and warmed with a few drops of dilute caustic soda solution. With *o*-aminobenzaldehyde, the reaction may be represented by the equation—

$$C_6H_4 <^{CHO}_{NH_2} + R' \cdot CO \cdot CH_2R$$
$$\rightarrow C_6H_4 <^{CH \, : \, CR}_{N \, : \, CR'} > + 2H_2O$$

in which R and R' can be hydrogen or alkyl radicles. As in the Doebner and Miller reaction, an aldol polymerisation probably ensues as an intermediate stage (Friedlaender, Ber. 1882, 15, 2574 ; Friedlaender and Göhring, *ibid.* 1883, 16, 1835 ; 1884, 17, 456).

From *o*-aminoacetophenone or *o*-aminobenzophenone and methyl alkyl ketones, under similar conditions, derivatives of 4-methyl- or 4-phenyl-quinoline can be produced (Geigy and Koenigs, Ber. 1885, 18, 2406 ; O. Fischer, *ibid.* 1886, 19, 1037).

Isatic acid also interacts similarly with ketones, their *isonitroso-* derivatives, ketonic acids or aldoximes, furnishing derivatives of quinoline-4-carboxylic (cinchonic) acid—

$$C_6H_4 <^{CO \cdot CH_3}_{NH_2} + R \cdot CO \cdot CH_3$$
$$\rightarrow C_6H_4 <^{C(CO_2H) \, : \, CH}_{N \, : \, CR} > + 2H_2O$$

(Pfitzinger, J. pr. Chem. 1885, [2] 33, 100 ; 1888, [2] 38, 582 ; 1897, [2] 56, 283 ; 1902, [2] 66, 263 ; Hübner, Ber. 1906, 39, 982).

(iii.) *Methods which give rise to the production of hydroxyquinolines containing the hydroxyl radicle in the 'pyridine' ring.*

The direct introduction of hydroxyl into the 'pyridine' ring of quinoline has been accomplished only in a few cases, such as the formation of carbostyril (2-hydroxyquinoline) by the action of hypochlorous acid on quinoline (Einhorn and Lauch, Ber. 1886, 19, 53 ; Erlenmeyer and Rosenhek, *ibid.* 1885, 18, 3295 ; 1886, 19, 498). Synthetical methods, however, have been devised for the production of 2- and 4-hydroxyquinolines, the most important of them being modifications of condensations already described.

From ethyl acetoacetate, derivatives of either 2-hydroxyquinoline or 4-hydroxyquinoline can be obtained by condensation with aniline, according as the anilide or the β-phenylaminocrotonate forms the intermediate product.

(1) **Knorr's synthesis.** The anilide, formed when a mixture of ethyl acetoacetate and aniline in molecular proportion is heated at 120°–150° under pressure for many hours,

they form quaternary ammonium compounds with methyl iodide.

AMINOQUINOLINES.

Of the aminoquinolines, six have been described. Those containing the NH_2 group in the 'benzene' ring can be obtained, either by reduction of the corresponding nitro-derivatives with tin and hydrochloric acid, or, like those containing it in the 'pyridine' ring, by heating the corresponding hydroxyquinoline with ammonio-zinc chloride.

2-Aminoquinoline is obtained by heating 2-chloroquinoline with ammonium carbonate and ammonia at 210° (Claus and Schaller, J. pr. Chem. 1897, [2] 56, 206), and from o-amino-cinnamonitrile $NH_2 \cdot C_6H_4 \cdot CH : CH \cdot CN$, by interaction with sodium ethoxide (Pschorr, Ber. 1898, 31, 1289). 4-Aminoquinoline can be prepared from cinchonamide by Hofmann's method (Wenzel, Monatsh. 1894, 15, 457). 3-Amino-quinoline has not been described.

The aminoquinolines are crystalline compounds, which act usually as mono-acid bases, give quaternary ammonium compounds with alkyl iodides, and are diazotisable, resembling in this respect primary aromatic amines.

QUINOLINESULPHONIC ACIDS.

On sulphonation with concentrated sulphuric acid at 220°–230°, quinoline yields the 8-sulphonic acid, but after many hours at 275°–280°, the 6-sulphonic acid (Georgievics, Monatsh. 1887, 8, 577, 639; Bad. Anilin- & Soda-Fab., D. R.-P. 40901 of 1887), both the 5- and the 8-sulphonic acids being converted into the 6-acid under these conditions (ibid.; Lellmann and Reusch, Ber. 1889, 22, 1391).

The 5- and 8- acids are obtained, but in proportions which depend on the temperature and concentration of the acid, when quinoline is heated with anhydrosulphuric acid at 120°–200°; the 8-acid predominates at lower, and the 5- acid at higher temperatures (Bedall and O. Fischer, Ber. 1882, 15, 683, 1979; [1] Riemerschmied, ibid. 1883, 16, 721; La Coste and Valeur, ibid. 1887, 20, 95). According to Claus, a third acid, the 7-sulphonic acid, is also present in the product at 125°–130°, but disappears as the temperature is raised (J. pr. Chem. 1888, [2] 37, 261). By further sulphonation with Nordhausen acid at 250°, a mixture of two disulphonic acids is produced (La Coste and Valeur, l.c.; La Coste, D. R.-P. 29920 of 1884.

For the preparation of the 5- acid, Skraup's method can be used (Lellmann and Lange, Ber. 1887, 20,'1446), and, by comparison of this acid with the 5- acid obtained by sulphonation under different conditions, Lellmann has drawn the conclusion that the latter exists in two forms (ibid. 2172; cf. Jakubowski, ibid. 1910, 43, 3026).

The quinolinesulphonic acids are crystalline, and can be separated from mixtures by fractional crystallisation of the calcium salts. They yield hydroxyquinolines by fusion with caustic alkali; nitriles by distillation with potassium cyanide; and di- or tri-bromoquinolines, with loss

[1] The 'meta'- acid described in these communications is the 5- not the 7- acid.

of the SO_3H group, on bromination in aqueous solution.

HYDROXYQUINOLINES.

Six of the seven hydroxyquinolines are known, viz. the 2- and 4- derivatives, and the four quinophenols, containing the OH group in the 'benzene' ring. From each, by combination with alkyl iodides, quaternary ammonium compounds are obtained.

The 2- and 4-hydroxyquinolines are produced either by synthetical methods (v. p. 473) or from the corresponding chloroquinolines by interaction with water at 120°. They exhibit the properties both of hydroxy- compounds and of ketonic derivatives, forming, for example, two series of ethers—

$$C_6H_4 \diagdown \begin{matrix} CH : CH- \\ N : C(OEt) \end{matrix} \diagup \qquad C_6H_4 \diagdown \begin{matrix} CH : CH \\ NEt : CH \end{matrix} \diagup$$

are less basic than the quinophenols; and are not reduced by tin and hydrochloric acid, but, in boiling alcoholic solution with sodium, eliminate the OH group forming tetrahydroquinoline.

The isomeric quinophenols can be prepared from aminophenols by Skraup's reaction; from aminoquinolines by the diazo- reaction; or from quinolinesulphonic acids by fusion with caustic alkali. They resemble the phenols or naphthols in properties, give only one series of ethers on alkylation, yield nitro- derivatives and sulphonic acids, and furnish stable salts with acids or alkalis. The 6- and 8-hydroxyquinolines, moreover, give nitroso- derivatives with nitrous acid, and couple with diazotised bases forming azo- dyes.

(i.) 2-**Hydroxyquinoline** (Carbostyril) is obtained when ethyl o-nitrocinnamate is reduced with alcoholic ammonium sulphide (Friedlaender and Ostermaier, Ber. 1881, 14, 1916); when o-aminocinnamic acid is boiled for some hours with hydrochloric acid (Tiemann and Oppermann, ibid. 1880, 13, 2070), or 50 p.c. sulphuric acid (Feer and Koenigs, ibid. 1885, 18, 2395); when 2-chloroquinoline is heated with water at 120° (Friedlaender and Ostermaier, ibid. 1882, 15, 335) or when quinoline is left in contact with bleaching-powder solution containing boric acid for some days (Erlenmeyer and Rosenhek, ibid. 1885, 18, 3295; Einhorn and Lauch, ibid. 1886, 19, 53); and, in 80 p.c. yield, when acetyl-o-aminobenzaldehyde in dilute (10 p.c.) alcoholic solution is boiled with one-third its weight of caustic soda (Camps, Arch. Pharm. 1899, 237, 682). Its occurrence in a sublimate collected from a furnace used for the ignition of sugar liquors has been noted by Lippmann (Ber. 1905, 38, 3829).

Properties.—It crystallises in prisms, or, from dilute aqueous solution with 1 mol. H_2O in needles, m.p. 199°–200°, is only sparingly soluble in cold water, and insoluble in ammonia, but dissolves in hydrochloric acid or caustic alkali solution. In many of its reactions, it has the properties of a phenol, in others those of a ketone (cf. Hartley and Dobbie, Chem. Soc. Trans. 1899, 75, 646); the corresponding ethers are known, the C-methyl ether, b.p. 246°–247° (Friedlaender and Weinberg, Ber. 1882, 15, 1422), and the N-methyl ether (1-methyl-2-quinolone), m.p. 74°, b.p. 324° (Friedlaender and

alkali, it is resolved into *quinaldine* and *phthalic acid*.

(2) When heated with alcoholic ammonia at 200° for 40 hours it is converted into *α-quinophthalin*, a basic yellow colouring matter (Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 27785 of 1883), forming garnet-red leaflets, m.p. 305° (Eibner and Hofmann, Ber. 1904, 37, 3021), isomeric with β-*quinophthalin*, pale yellow prisms,

(α) $C_6H_4 <^{CO}_{C(NH)}> CH \cdot C_9H_6N$

(β) $C_6H_4 <^{CO}_{C(CH \cdot C_9H_6N)}> NH$

m.p. 213°, obtained by adding phthalimide to a mixture of quinaldine and zinc chloride at 160°–180° (Eibner and Lange, *l.c.*; Eibner and Hofmann, *l.c.*).

(3) It dissolves in sulphuric acid, but is sulphonated by anhydrosulphuric acid in the cold, forming **quinoline-yellow**, which consists of a mixture of quinophthalonemono- and di-sulphonic acids; the sodium salt, obtained from this product, is a soluble yellow powder, which dyes wool a fast greenish-yellow in an acid bath.

*iso*Quinophthalone (unsym-*quinophthalone*, 2-*quinaldylene-phthalide*; Formula II), formed when the quinophthalone reaction (p. 482) is carried out at a temperature not exceeding 180° crystallises in orange-yellow prisms, m.p. 1 dissolves only sparingly in alcohol but easily in chloroform, and when heated at 240°–250°, with benzaldehyde, or with sodium converted into *quinophthalone*. On with alcoholic ammonia at 100°, it furnishes *quinaldine* and *phthalamide*; and with anhydro-sulphuric acid at 100°, it forms quinoline-yellow (Eibner and Merkel, Ber. 1902, 35, 2297; *cf.* 1904, 37, 3008).

Homologues of both *sym*- and *unsym*-quinophthalone have been prepared, and these increase in intensity, fastness to light, covering power, and insolubility in alcohol with increase in molecular weight (Eibner and Hofmann, Ber. 1904, 37, 3017; Eibner, D. R.-P. 158781 of 1903).

By the substitution of β-thiophthalic acid for phthalic anhydride in these condensations, compounds are obtained which dye unmordanted cotton in yellow shades, and on oxidation by the air or with dichromate give very fast colours (Gesellsch. chem. Ind. Basel, D. R.-P. 189943 of 1906; Eng. Pat. 4159 of 1907). The condensation product from 6-chloroquinaldine and phthalic anhydride on sulphonation furnishes a greenish-yellow dye for silk or wool (Farbenfab. vorm. F. Bayer & Co., D. R.-P. 204255 of 1907; Eng. Pat. 28266 of 1908).

*iso*Quinoline. This base is a constituent of coal-tar quinoline, and can be isolated from this source by taking advantage of the fact that the acid sulphates of quinoline and quinaldine are more soluble in alcohol than the isoquinoline salt. The crystalline sulphate, which separates from an alcoholic solution of the acid sulphates of coal-tar quinoline, is decomposed by caustic potash,

and the fraction, b.p. 236°–243°, reconverted into acid sulphate, is repeatedly crystallised from twice its weight of 88 p.c. alcohol until the m.p. rises to 205° (Hoogewerff and van Dorp, Rec. trav. chim. 1885, 4, 125, 285; 1886, 5, 305; *cf.* Dewar, Roy. Soc. Proc. 1880, 30, 167).

Syntheses.—The methods devised for the synthesis of *iso*quinoline and its derivatives are less general in their scope than those employed in the quinoline series. The following are perhaps the most important of these methods, as they serve both to throw light on the constitution of *iso*quinoline, and to illustrate the connection between this base and the alkaloids.

(1) The first synthesis of *iso*quinoline was effected by heating homophthalimide with phosphorus pentachloride, the dichloro*iso*quinoline thus formed being then reduced by hydriodic acid and phosphorus—

$C_6H_4 <^{CH_2 \cdot CO}_{CO \cdot NH}>$ $C_6H_4 <^{CH : CCl}_{CCl : N}>$

$C_6H_4 <^{CH : CH}_{CH : N}>$

(Gabriel, Ber. 1886, 19, 1655, 2361).

(2) *iso*Quinoline has been obtained by heating with zinc dust, homophthalimide (Le Blanc, Ber. 1888, 21, 2299); *iso*carbostyril (Bamberger and Kitschelt, *ibid.* 1892, 25, 1147); or *iso*carbostyrilcarboxylic acid (Zincke, *ibid.* 1497; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 65947 of 1892)

$C_6H_4 <^{CH : CH}_{CO : NH}> + Zn$

$\rightarrow C_6H_4 <^{CH : CH}_{CH : N}> + ZnO.$

*iso*Carbostyril and certain of its derivatives can be synthesised from *iso*cumarin and its derivatives by condensation with ammonia, methylamine or aniline in cold aqueous or warm alcoholic solution

$C_6H_4 <^{CH : CR}_{CO \cdot O}> + NH_3$

$\rightarrow C_6H_4 <^{CH : CR}_{CO \cdot NH}> + H_2O$

(Bamberger and Kitschelt, *l.c.*; Zincke, *l.c.*; Bamberger and Frew, Ber. 1894, 27, 198); or they may be obtained from diacyl derivatives of o-cyanobenzyl cyanide (homophthalimide) by warming these with alkalis and boiling the resulting cyano*iso*carbostyril with sulphuric acid (Gabriel and Neumann, Ber. 1892, 25, 3563; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 69138 of 1892; Damerow, Ber. 1894, 27, 2322).

(3) It is formed by dissolving benzylamino-acetaldehyde in anhydrosulphuric acid (E. Fischer, Ber. 1893, 26, 764), or by heating benzylideneaminoacetal with sulphuric acid at 150°–170° (Pomeranz, Monatsh. 1893, 14, 118; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 80044 of 1894).

$C_6H_4 <^{H}_{CH_2 \cdot NH \cdot CH_2 \cdot CHO}$

$\rightarrow C_6H_4 <^{CH : CH}_{CH : N}> + H_2 + H_2O$

Derivatives of *iso*quinoline are obtained by condensing aminoacetal in sulphuric acid solution with acetophenone (Pomeranz, Monatsh.

nitroso- derivative, needles, m.p. 53°, an *acetyl* derivative, m.p. 46°, and in its properties shows much resemblance to benzylamine (Bamberger and Dieckmann, *l.c.*). The *hydrochloride*, B·HCl, forms prisms, m.p. 195°–197°; the *platini-chloride*, $B_2 \cdot H_2PtCl_6$, prisms, m.p. 231°–232°; and the *picrate*, needles, m.p. 195°. For the 2-alkyl derivatives, *cf.* Wedekind and Oechslen, Ber. 1901, 34, 2986.

Only one colouring matter has been obtained from *iso*quinoline, namely—

*iso*Quinoline-red, $C_{26}H_{19}N_2Cl$. This dye was obtained originally by heating benzotrichloride, benzochlorodibromide, or benzylidene chloride with a mixture of coal-tar quinoline and zinc chloride (Jacobsen, D. R.-P. 19306; 23967; Eng. Pat. 814 of 1882); and is formed by the interaction of benzotrichloride, *iso*quinoline, and quinaldine in mol. prop., either at 150°, or more rapidly in the presence of zinc chloride at 120° (Hofmann, Ber. 1887, 20, 9). The quinaldine cannot be replaced by lepidine (Vongerichten and Homann, Ber. 1912, 45, 3447).

Preparation.—A yield of 25–30 p.c. of the dye is obtained, if benzotrichloride (38 pts.) is added slowly to a mixture of *iso*quinoline (25 pts.), quinaldine (26 pts.), and zinc chloride (12·5 pts.) at 100°, and the temperature afterwards raised to 150°. Much hydrogen chloride escapes, and the reaction needs watching lest it become violent. From the extract of the product with 10 p.c. milk of lime, the unchanged bases are removed by steam, the filtrate being then acidified with hydrochloric acid to separate the dyestuff (Vongerichten and Homann, *l.c.* 3449; *cf.* Actieng. für Anilinfab., D. R.-P. 40420 of 1886).

Properties.—*iso*Quinoline-red forms dark red, bronze-lustred, monoclinic prisms, which dissolve only sparingly in cold water, but readily in hot water or alcohol; these solutions are carmine-red by transmitted light, and in reflected light show a marked yellowish-red fluorescence. When heated with hydrochloric acid or with alcoholic ammonium sulphide at 200° it yields *benzaldehyde* or *benzylmercaptan* respectively, and a *base* $C_{19}H_{14}N_2$, which crystallises in plates of golden lustre, m.p. 231° (Hofmann, *l.c.*; *cf.* Vongerichten and Homann, *l.c.*). By oxidation with potassium dichromate and sulphuric acid, it furnishes *benzaldehyde* and 2-*quinolyl*-1-*iso*quinolyl ketone (Vongerichten and Krantz, Ber. 1910, 43, 129; Vongerichten and Homann, *l.c.*). As a dye-stuff it is valueless, the rose-red shades on silk or wool not being fast to light; but, mixed with cyanine, it has been used in the preparation of orthochromatic ('azaline') plates for photographic purposes (Vogel. D. R.-P. 39779 of 1886). W. P. W.

QUINOLINE DYES *v.* QUINOLINE.

QUINOLINIC ACID *v.* BONE OIL.

QUINONE DIAZIDES (*cyclic diazo-oxides*) *v.* DIAZO COMPOUNDS.

QUINONES are substances derived from aromatic hydrocarbons by replacement of two hydrogen by two oxygen atoms. The earliest known member of the series, *para*benzoquinone (or simply quinone) was obtained by the oxidation of various substituted benzenes

(Woskresensky, Annalen, 1838, 27, 268; Wöhler, *ibid.* 1844, 51, 152); since it yields hexachlorobenzene when treated with phosphorus pentachloride, is easily reduced to *p*-dihydroxybenzene (quinol), and may be obtained from the latter by oxidising agents, the formula of a *p*-phenylene peroxide was assigned to it (Graebe, *ibid.* 1868, 146, 1). The relationship between quinone and quinol can then be represented by—

At a later date it was found that whilst benzene was reduced by free hydroxylamine, the hydrochloride gave an oxime which proved to be identical with *p*-nitrosophenol (Goldschmidt, Ber. 1884, 17, 805). The monoxime gave in turn a dioxime, these reactions pointing to the following respective formulæ for quinone, its mono- and its di- oximes.

The constitution of quinone-oxime itself cannot be taken as absolutely settled; according to C. H. Sluiter (Rec. trav. chim. 1906, 25, 8), the free substance is *p*-nitrosophenol whilst the salts are derived from the quinone-oxime.

Additional support for the diketonic formula is afforded by the production of trichloroacetylacrylic acid when chlorous acid acts on benzene, quinone, &c. (Kekulé and Strecker, Annalen, 1884, 223, 170)—

and by the production of bromanil (tetrabromoquinone) from bromine and *cyclo*-hexane-1 : 4-dione

Ortho-quinones, *e.g.*

were discovered at a later date; metaquinones have not so far been obtained (R. Meyer and Desamari, Ber. 1908, 41, 2437; Zincke and Schwabe, *ibid.* 1909, 42, 797), it is doubtful whether they are capable of existence.

Within the last few years a number of

Discovered by Rio de la Loza in the Mexican drug *Raíz del Pipitzahuac* or *Radix Pereziae*; m.p. 104°. Yields *anilino-* and *hydroxy-* derivatives (Weld, Annalen, 1855, 95, 188; Anschütz, Ber. 1885, 18, 709; Annalen, 1887, 237, 90; Fichter, Jetzer and Leepin, *ibid.* 1913, 395, 15).

Phenyl-p-benzoquinone $C_6H_3(C_6H_5)O_2$ is obtained by oxidation of 5-amino-2-hydroxy-diphenyl with chromic acid mixture (Borsche, Ber. 1899, 32, 2937; Annalen, 1900, 312, 220; Hill and Hale, Ber. 1900, 33, 1242); m.p. 112°–113°. Several derivatives are known; *see* also Jackson and Koch (Amer. Chem. J. 1901, 26, 23). Phenylbenzoquinone is isomeric with diphenoquinone $O : C_6H_4 : C_6H_4 : O$ (*vide infra*).

1 : 3-Diphenyl-2 : 5-benzoquinone

$$C_6H_2(C_6H_5)_2O_2,$$

m.p. 137°–138° (Borsche, Ber. 1899, 32, 2938: Annalen. 1900, 312. 230); m.p. 135°–136° (corr.) (Hill, Amer. Chem. J. 1900, 24. 8; Hill and Soch, Ber. 1900, 33, 1241). The *monoxime* and its benzoyl derivative have been prepared, whilst 4-*anilino-*1 : 3-diphenylbenzo-2 : 5-quinone m.p. 167°, is formed when the quinone is boiled with aniline.

1 : 4-Diphenyl-2 : 5-benzoquinone

$$C_6H_2(C_6H_5)_2O_2,$$

m.p. 214°. By alkaline condensation of methyl-phenyldiketone. Orange yellow leaflets (Müller and von Pechmann, Ber. 1889, 22, 2131). Diphenyldihydroxy-p-benzoquinone and Dibenzyldihydroxy-p-benzoquinone (Fichter, Annalen, 1908, 361, 363).

1 : 4-Dibenzhydryl-2 : 5-benzoquinone

$$C_6H_2[CH(C_6H_5)_2]_2O_2.$$

By condensation of benzoquinone with benzhydrol, m.p. 250° (indef.) (Möhlau, Ber. 1898, 31. 2351; Möhlau and Klopfer, *ibid.* 1899, 32, 2147). The *octamethyltetraamino-* derivative

$$C_6H_2[CH\{C_6H_4.N(CH_3)_2\}_2]_2$$

is obtained by warming benzoquinone with Michler's hydrol for 6 hours in alcoholic solution; m.p. 245°.

Other substituted benzoquinones are obtained by the action of substances of the indole series on quinone. Thus α-methylindole reacts as follows :

e.g. α-*methylindyl*-p-*benzoquinone*, m.p. 185°. N-*methyl* - α - *methylindyl* - p - *benzoquinone*, m.p. 160°; α-*phenylindyl*-p-*benzoquinone*, m.p. 205°, and other substances. Tetrahydroquinoline also reacts, giving $C_6H_2(C_9H_{10}N)_2O_2$, m.p. 189° (Möhlau and Redlich, Ber. 1911, 44, 3605).

QUINONES $C_nH_{2n-14}O_2.$

Naphthaquinones. Six naphthaquinones are possible

The 1 : 2-, 1 : 4-, and 2 : 6-quinones have been prepared. The first two have been known for a long period, the 2 : 6-quinone was obtained by Willstätter and Parnas (Ber. 1907, 40, 1406, 3971). See article on NAPHTHALENE.

QUINONES $C_nH_{2n-16}O_2.$

Phenylquinone $C_6H_3(C_6H_5)O_2$ is dealt with earlier in this article.

QUINONES $C_nH_{2n-18}O_2.$

Acenaphthenequinone $C_{12}H_6O_2$, or

CO–CO

m.p. 262°–263°.

This compound is not strictly a quinone, the two carbonyl groups being situated in a 5-membered ring. It has been prepared by oxidation of acenaphthene $C_{12}H_{10}$ with chromic acid mixture, &c.; the yields are not, however, good (Graebe, Ber. 1887, 20, 659; Graebe and Gfeller, *ibid.* 1892, 25, 654; Annalen, 1893, 276, 1). Better results have been obtained by hydrolysing the monooxime obtained by the action of alkyl nitrites on acenaphthene.

When four molecular proportions of amyl nitrite are added to a boiling solution of acenaphthene whilst a stream of hydrogen chloride is passed in, two isomeric acenaphthenequinone-oximes $C_{12}H_6(:NOH)O$ are produced. These may be separated by difference of acidity, one being insoluble in hot sodium carbonate solution. When this is rapidly crystallised from glacial acetic acid, small pale yellow crystals which decompose at 207° are obtained. If the boiling with acetic acid be continued some time, water precipitates the oxime of m.p. 230°, which can be obtained from acenaphthenequinone and hydroxylamine (Francesconi and Pirazzoli, Gazz. chim. ital. 1903, 33, i. 42).

To prepare acenaphthene quinone, the oxime of higher m.p. is dissolved in 7 times its weight of 75 p.c. sulphuric acid and heated for 1 hour on the water-bath. Water is added, the quinone filtered off, digested for some time with warm dilute caustic soda and recrystallised from glacial acetic acid (Kalle and Co., D. R. P. 228698, 1909; Reissert, Ber. 1911, 44, 1749). For the oxime, m.p. 220° is given.

Acenaphthene quinone yields a compound $C_{12}H_6(C_6H_5)_2O$ (diphenylacenaphthenone) with benzene and aluminium chloride (Zsuffa, Ber. 1910, 43. 2915); on reduction compounds of m.p. 248° and 254° are produced (Kalle and Co.,

QUINONES $C_nH_{2n-18}O_2$.

Many quinones $C_{18}H_{10}O_2$ are possible and the following have been obtained.

Naphthacenequinone.   1 : 2-Chrysoquinone.

2 : 3-Chrysoquinone.   Naphthanthraquinone.

Naphthacenequinone $C_{18}H_{10}O_2$, is a para-quinone showing considerable analogy to anthra-quinone: it is derived from a parent hydro-carbon naphthacene $C_{18}H_{12}$. The constitutional formulæ of these two compounds and the method of numbering the positions in the naphthacene quinone molecule are shown below.

Naphthacene.   Naphthacenequinone.

Gabriel and Michael melted a mixture of phthalic anhydride, succinic acid and fused sodium acetate and obtained ethylene (di)phtha-lide (Ber. 1877, 10, 1558)

$$2C_6H_4\!\!<^{CO}_{CO}\!\!>O + {}^{CH_2\cdot CO_2H}_{CH_2\cdot CO_2H}$$

$$= 2CO_2 + 2H_2O + C_6H_4\!\!<^{C=CH\cdot CH=C}_{CO}\!\!>O\quad O\!\!<^{}_{CO}\!\!>C_6H_4$$

Roser examined the reaction and found that an *iso*-ethylene diphthalide was formed at the same time in small quantity (Ber. 1884, 17, 2774). Gabriel and Leupold improved the method for obtaining the ethylene phthalide (*ibid.* 1898, 31, 1161) and also examined the action of sodium methoxide on ethylene di-phthalide which had been previously studied by F. Nathanson (*ibid.* 1893, 26, 2582). Nathanson suspended ethylene phthalide in methyl alcohol, added sodium methoxide, evaporated off the methyl alcohol, added hot water, separated from undissolved mattter and precipitated the filtrate with hydrochloric acid. The substance so obtained gave results on analysis agreeing with the expected *bis*-diketohydrindene,

$$C_6H_4\!\!<^{CO}_{CO}\!\!>CH\cdot CH\!\!<^{CO}_{CO}\!\!>C_6H_4.$$

Gabriel and Leupold recognised that Roser's *iso*ethylene diphthalide was also formed in the reaction (Ber. 1898, 31, 1272) and found that it contained two hydroxyl groups. On distillation with zinc dust, hydrocarbons $C_{14}H_{12}$ and $C_{18}H_{14}$ were obtained. The latter evidently contains two CH_2-groups, since on oxidation with chromic acid, a quinone $C_{18}H_{10}O_2$ is produced. This quinone when fused with potash gives benzoic

and β-naphthoic acids (anthraquinone when fused with potash gives two molecules of benzoic acid (Graebe and Liebermann, Annalen, 1871, 160, 129), which points to the formula given above for naphthacenequinone. The 'isoethylenediphthalide' was found to contain two hydroxyl groups. It can be formulated as a dihydroxynaphthacene quinone, and its pro-duction from ethylene diphthalide explained in the following manner.

$$\overset{C\quad CH\ CO}{\underset{CO\quad CH=C}{\bigcirc O \mid O\bigcirc}} + Na_2O + NaOH$$

$$= \overset{ONa}{\underset{ONa}{\bigcirc}}\overset{C=CH}{\underset{CO}{\quad}}\overset{NaO\cdot CO}{\underset{CH_2=CO}{\quad}}$$

$$= NaOH + H_2O + \overset{ONa}{\underset{C\ CO}{\bigcirc}}\overset{}{\underset{C\ CO}{\quad}}$$
$$\qquad\qquad\qquad ONa$$

Another method for the production of naphthacenequinone derivatives was intro-duced by Deichler and Weizmann (Ber. 1903, 36, 547) who condensed α-naphthol with phthalic acid in presence of concentrated sul-phuric acid.

$$\overset{COOH}{\underset{COOH}{\bigcirc}} + \overset{OH}{\bigcirc} = 2H_2O + \overset{CO\ OH}{\underset{CO}{\bigcirc}}$$

Naphthacenequinone $C_{18}H_{10}O_2$. By oxidising 6 grms. of dihydronaphthacene in 360 c.c. of glacial acetic acid with 9 grms. of chromic acid dissolved in 9 c.c. of water and 90 c.c. of glacial acetic acid. Long yellow needles, m.p. 294° (Gabriel and Leupold, Ber. 1898, 31, 1277).

1 - Chloronaphthacenequinone $C_{18}H_9ClO_2$. From hydroxynaphthacene quinone and phos-phorus pentachloride, m.p. 254° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 118).

1 : 6-Dichloronaphthacenequinone $C_{18}H_8Cl_2O_2$. From dihydroxynaphthacene quinone and phos-phorus pentachloride, m.p. 259°-260° (Gabriel and Leupold, Ber. 1898, 31, 1282).

Bromo-1-chloronaphthacenequinone $C_{18}H_8ClBrO_2$, m.p. 180° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 119).

Nitronaphthacenequinone $C_{18}H_9(NO_2)O_2$. By nitration of naphthacene quinone, m.p. 315° (Gabriel and Leupold, *l.c.* 1278).

Dinitronaphthacenequinone $C_{18}H_8(NO_2)_2O_2$, from dihydronaphthacene and nitric acid, m.p. 40° (*ibid.*).

1-Hydroxynaphthacenequinone $C_{18}H_9(OH)O_4$. Prepared by intimately mixing 50 grms. of

1 : 4 : 5-Trihydroxynaphthacenequinone ?

$$C_{18}H_7(OH)_3O_2$$

does not melt below 360°. The solutions in cold sodium carbonate and concentrated sulphuric acid are cornflower-blue in colour (Bentley, Friedl and Weizmann, *ibid.* 1907, 91, 1593).

Trihydroxynaphthacenequinones have also been prepared by fusing 1 : 6-dihydroxynaphthacenequinone with alkali (Deichler and Weizmann, Ber. 1903, 36, 725) and by alkaline fusion of the sulphonic acid obtained from 1 : 6-aminohydroxynaphthacene quinone (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 417).

1-Aminonaphthacenequinone

$$C_{18}H_9(NH_2)O_2.$$

From hydroxynaphthacene quinone and ammonia ; m.p. 290°–292° (*ibid.* 415).

1-Amino-6-hydroxynaphthacenequinone

$$C_{18}H_8(NH_2)(OH)O_2.$$

By reduction of the nitro compound (Deichler and Weizmann, Ber. 1903, 36, 2328; Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 121; Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 417).

7 : 10-Dichloro-1-hydroxy-6-aminonaphthacenequinone $C_{18}H_6Cl_2(OH)(NH_2)O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 284).

1-Anilino-6-hydroxynaphthacenequinone

$$C_{18}H_8(NHC_6H_5)(OH)O_2$$

and its *acetyl derivative* (Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 419).

2 ?-Nitro-6 ?-anilino-1-hydroxynaphthacenequinone $C_{18}H_7(NO_2)(NHC_6H_5)(OH)O_2$ (*ibid.* 420).

7 (or 10)-Chloro-10 (or 7)-anilino-1-hydroxynaphthacenequinone

$$C_{18}H_7Cl(NHC_6H_5)(OH)O_2$$

(Harrop and Weizmann, *ibid.* 1909, 95, 285).

1-Amino-6 : 8 (or 9)-dihydroxynaphthacenequinone $C_{18}H_7(NH_2)(OH)_2O_2$ (*ibid.* 423).

1 : 6-Dianilinonaphthacenequinone

$$C_{18}H_8(NHC_6H_5)_2O_2.$$

By the action of aniline on dichloronaphthacene quinone (Gabriel and Leupold, Ber. 1898, 31, 1283).

8 : 9-Dichloro-7 : 10-dianilino-1-hydroxynaphthacenequinone

$$C_{18}H_5Cl_2(NHC_6H_5)_2(OH)O_2$$

(Harrop and Weizmann, Chem. Soc. Trans. 1909, 95, 288).

7 : 10-Dianilino-1 : 5-dihydroxynaphthacenequinone $C_{18}H_6(NHC_6H_5)_2(OH)_2O_2$ (*ibid.* 285).

8 : 9-Dichloro-7 : 10-dianilino-1 : 6-dihydroxynaphthacenequinone

$$C_{18}H_4Cl_2(NHC_6H_5)_2(OH)_2O_2$$

(*ibid.* 288).

Naphthacene-diquinone

$$C_6H_4\underset{CO}{\overset{CO}{<}}{>}C_2\underset{CO}{\overset{CO}{<}}{>}C_6H_4$$

is obtained by the action of nitric acid on 1 : 6-dihydroxynaphthacene quinone. Sinters at 325°, m.p. 330°–333° (Gabriel and Leupold, Ber. 1898, 31, 1283).

The action of halogens on naphthacene-diquinone has been examined by Voswinckel (Ber.

1905, 38, 4015). The colourless dichloride, $C_{18}H_8O_4Cl_2$, of m.p. 175°, gives the acid

when treated with soda. With bromine, trihydroxynaphthacenequinone bromide

m.p. 198°, is obtained, whilst bleaching powder gives an oxide

melting about 240°.

Voswinckel draws attention to the fact that several compounds which have been described at different times belong probably to the naphthacenequinone series (*e.g.* dibenzoyl-succinic dianhydride, L. Knorr and Scheidt, Annalen, 1896, 293, 74).

1 : 2-Chrysoquinone $C_{18}H_{10}O_2$.

By oxidation of chrysene with chromic acid (Liebermann, Annalen, 1871, 158, 309; Graebe, Ber. 1874, 7, 784; Bamberger and Burgdorf. *ibid.* 1890, 23, 2437; Schmidt, J. pr. Chem. 1874, [ii.] 9, 284; Graebe and Hönigsberger, Annalen, 1900, 311, 262). Crystallises in needles from toluene and benzene or in plates from hot glacial acetic acid : m.p. (corr.) 239·5°. *Monooxime*, m.p. 160°–161° (Graebe and Hönigsberger).

The reactions of chrysoquinone resemble those of phenanthraquinone. Derivatives have been described by Liebermann (*l.c.*); Adler (Ber. 1879, 12, 1892): Japp and Streatfeild (Chem. Soc. Trans, 1882, 41, 157) and Abegg (Ber. 1891, 24, 953).

2 : 8- or *amphi*-Chrysoquinone.

By oxidising 2 : 8-dihydroxychrysene in boiling glacial acetic acid with lead peroxide. Reddish-yellow needles m.p. 288°–290°. *Compound*

$$C_{18}H_{10}O_2 \cdot NaHSO_3 \cdot 2H_2O.$$

Oxidised by air in hot alcoholic suspension to 8-hydroxy-1 : 2 chrysoquinone, dark-red needles which decompose above 300°. Gives 8-hydroxy-1 : 2-chrysoquinone-1-phenylimine, m.p. 230°, on treatment with aniline (Beschke and Diehm, Annalen, 1911, 384, 173).

Naphthanthraquinone $C_6H_4\underset{CO(2)}{\overset{CO(1)}{<}}{>}C_{10}H_6.$

From naphthoyl-*o*-benzoic acid and concentrated sulphuric acid. Constitution, Gabriel and Colman (Ber. 1900, 33, 449). *Mononitro-derivatives*, &c. (R. Scholl, *ibid.* 1911, 44, 2370, 2992; Monatsh. 1912, 33, 507).

QUINONES $C_nH_{2n-32}O_2$.

Dinaphthanthraquinone

$$C_{10}H_6\underset{(3)\cdot CO\cdot(3)}{\overset{(2)\cdot CO\cdot(2)}{<}}{>}C_{10}H_6,$$

Tetrabromostilbenequinone

...

2 : 5 : 2 : 5 -Tetrabromo-3 : 3 -dimethylthiolstilbene-4 : 4 -quinone

...

DERIVATIVES OF AZOBENZENE.

Azobenzenequinone. or quinone azine

$$O : C_6H_4 : N \cdot N : C_6H_4 : O.$$

...

$$C_{12}H_{10}O_4N_2.$$

...

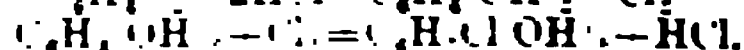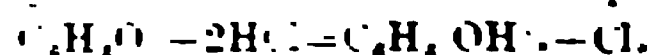## ADDITION COMPOUNDS OF QUINONES.

MERIQUINONOID COMPOUNDS.

A large number of substances are known in which quinonoid and benzenoid compounds have entered into a somewhat loose combination. The earliest-known member of this group was *quinhydrone*, a strongly coloured equimolecular compound of quinone and quinol discovered by Wöhler in 1844 (Annalen, 51, 153). The term quinhydrone is now used generically for the addition products of quinones and phenols, but since similar addition products of quinone-diammonium salts with aromatic diamines

...

A somewhat similar idea is to be found in the formulation of quinhydrone as

(G. Urban, Monatsh. 1907, 28, 290); Willstätter and Piccard (l.c.) 1464, footnote, point out that this does not take into account the salt formation of the quinhydrones.

M. M. Richter, who formulates the addition product of hydrogen persulphide and quinone as

$$H\cdot O\cdot S\cdot S\cdot S\cdot O\cdot H$$

thinks the quinhydrones are also oxonium compounds. Three oxonium formulæ

are possible for ordinary quinhydrone of which the second is preferred (Ber. 1910, 43, 3603). This view does not commend itself to Angelo Knorr (ibid. 1911, 44, 1503). The true imonium compound obtained from quinone-diimine and p-nitrophenol (m.p. 59°) is yellow, i.e. has not the marked colour associated with quinhydrones.

The meriquinonoid compounds obtained from bases were frequently mistaken for the quinonoid substances themselves.

Jackson and Calhane acted on p-phenylenediamine and its dibromo-derivative with bromine, obtaining deeply coloured salts which they considered were compounds of the diimines

$$C_6H_4(:NH)_2 \text{ and } C_6H_2Br_2(:NH)_2$$

(Ber. 1902, 35, 2495). Subsequently it was

found that quinone-imine and quinone-diimine were colourless substances and gave colourless salts if in a state of purity (Willstätter and Pfannenstiehl, Ber. 1904, 37, 4606). Kehrmann suggested that many of the deeply coloured oxidation products obtained from simple amines might be of quinhydrone type (ibid. 1905, 38, 3777). A careful examination by Willstätter and Piccard (ibid. 1908, 41, 1458) of the oxidation products obtainable from dimethyl-p-phenylene diamine showed that whilst the completely quinonoid nitrate

$$HNO_3\cdot HN : C_6H_4 : N(CH_3)_2NO_3$$

was colourless, the coloured salts obtained by Wurster (Ber. 1879, 12, 1803, 1807, 2071) and considered by Bernthsen (Annalen, 1885, 230, 162; 1889, 251, 11, 49, 82) to be wholly quinonoid, are actually of meriquinonoid type. Wurster's red must be considered as an addition product

$$BrNH_2 : C_6H_4 : N(CH_3)_2Br + NH_2\cdot C_6H_4\cdot N(CH_3)_2.$$

Kehrmann (Ber. 1908, 41, 2340), and Schlenk and Knorr both draw attention to the fact that quinhydrones are dissociated into their constituents in solution, but Wurster's red is not. Evidently the firmness of union of quinonoid and benzenoid molecules varies in degree (Willstätter and Piccard, Ber. 1909, 42, 1902).

Jean Piccard (Annalen, 1911, 381, 351) has shown that the meriquinonediimonium salts

$$NH_2Br : C_6H_4 : NH_2Br + NH_2\cdot C_6H_4\cdot NH_2$$

exist in two modifications, α and β. The α-compounds are formed preferably in presence of alcohol; the β-salts, which are polymers and more strongly coloured, at low temperatures, in presence of water. The β-form is usually the more stable.

Some of the addition products formed by quinones and quinonoid compounds are given in the following list. The figures in brackets refer to the number of molecules of reacting substances, e.g.:—
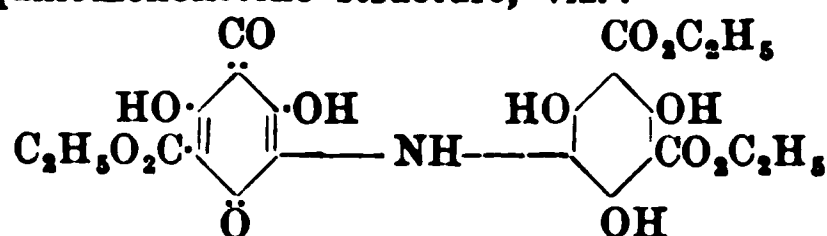
(3) $1:4\cdot C_6H_4O_2+(4)1:2:3$ $C_6H_3(OH)_3$,

        m.p. 78°, Siegmund,

means that Siegmund has prepared an addition product of 3 molecules of p-benzoquinone with 4 molecules of pyrogallol which melts at 78°.
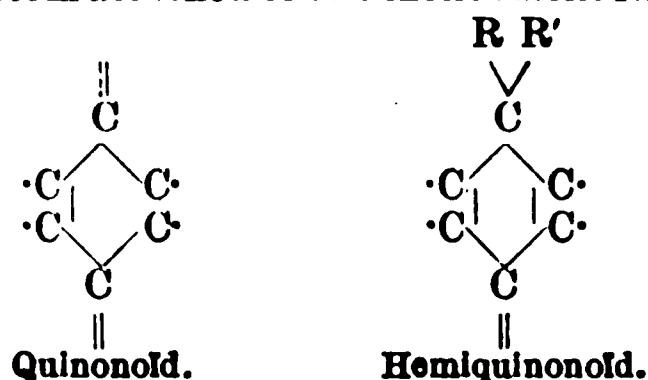
a substance is, however, known to which a quinomonoketene structure, viz.:—

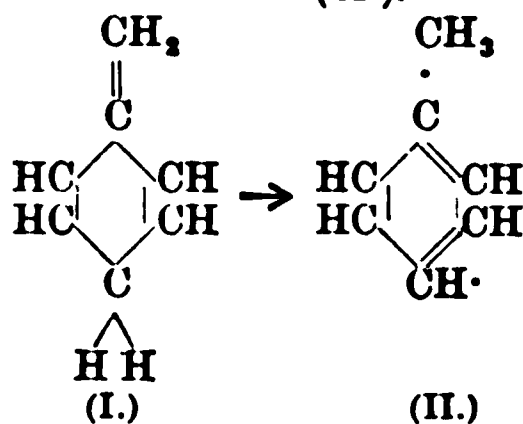has been ascribed (Leuchs and Theodorescu, Ber. 1910, 43, 1239).

HEMIQUINOÏD COMPOUNDS.

Several compounds already referred to contain a grouping which can be described as hemiquinonoïd. The cyclo-hexadiene ring is intact but the carbonyl group (or its equivalent $>C:N-$, $>C:C<$) is only found once, the other carbonyl group being represented by a carbon atom attached to two monovalent radicles
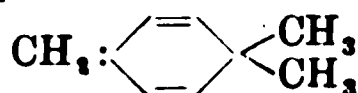

Quinonoïd.   Hemiquinonoïd.

HYDROCARBONS.

Instead of the term 'hemiquinonoïd,' Auwers refers to compounds of this type as 'semi-benzenoïd.' The parent substance of the group would be a hydrocarbon of structure (I). It is probably incapable of existence, and any reactions devised for obtaining it would result in the production of toluene (II.).
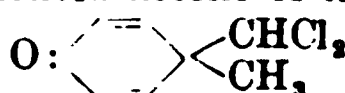

(I.)   (II.)

A dimethyl derivative shows sufficient stability for isolation (Auwers and K. Müller, Ber. 1911, 44, 1595).
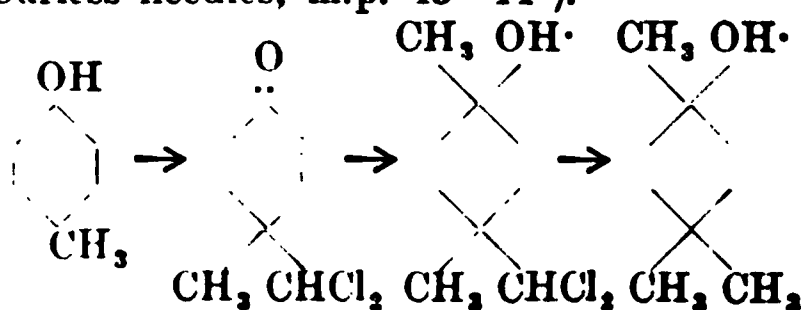
1 : 1-Dimethyl-4-methylene cyclo- $\Delta^{2,5}$-hexadiene C_9H_{12} or

A hemiquinonoïd ketone of the structure

is prepared by the action of chloroform and sodium hydroxide on p-cresol (Ber. 1905, 38, 1705). This reacts normally with magnesium methyliodide, yielding a carbinol which need not be isolated before reduction in moist ether-alcohol solution to trimethyl-cyclo-hexadiene-ol (colourless needles, m.p. 43°-44°).
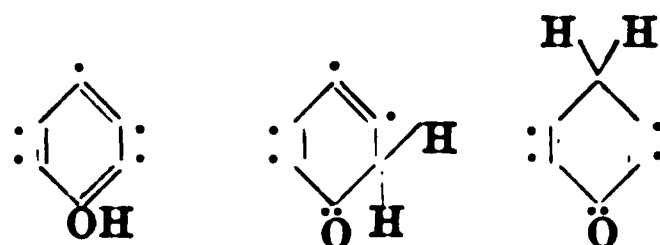

The carbinol loses a molecule of water when shaken for 20 minutes with 10 p.c. sulphuric acid and ice. The resulting 1 : 1-dimethyl-4-methylene-cyclo-$\Delta^{2,5}$-hexadiene is extracted with ether, the ethereal extract dried over calcium chloride and distilled under reduced pressure : b.p. 50° at 23 mm. ; unstable. The molecular refraction and dispersion are far higher than for the isomeric benzenoïd compounds (mesitylene, pseudo-cumene and methylethylbenzene).

Other papers by Auwers on compounds of ' semibenzene ' type may be referred to (Ber. 1903, 36, 1861, 3902; 1905, 38, 1697; 1906, 39, 3748; Annalen, 1907, 352, 219, 273, 288; Ber. 1910, 43, 3094; 1911, 44, 588, 788, 1595, 3679).
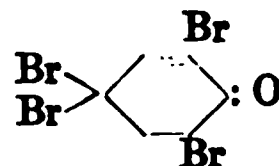
PSEUDOPHENOLS.

If the idea of keto-enolic tautomerism is extended to the phenols, each hydroxy-derivative of benzene corresponds to two ketocyclohexadienes
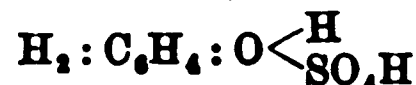

In the case of phenol and its simpler derivatives, the possibility of isolating desmotropic forms appears to be remote, the tribromophenol bromide $C_6H_2OBr_4$, obtained by adding strong bromine water to a solution of phenol in 600–1000 parts of water, and to which Benedikt (Annalen, 1879, 199, 128; Monatsh. 1880, 1, 360) assigned the constitution
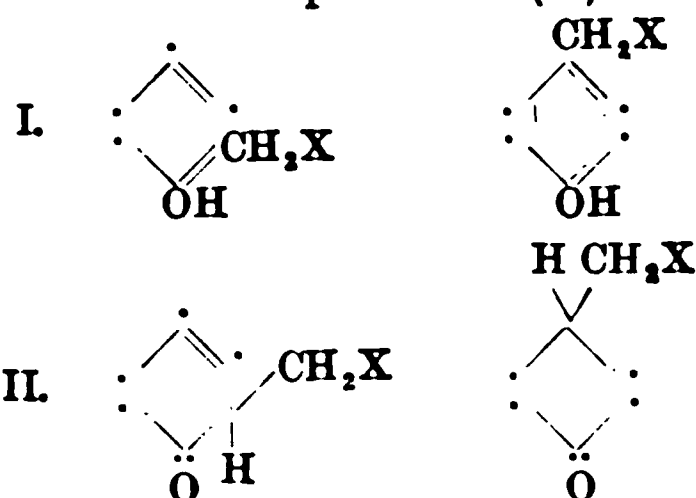
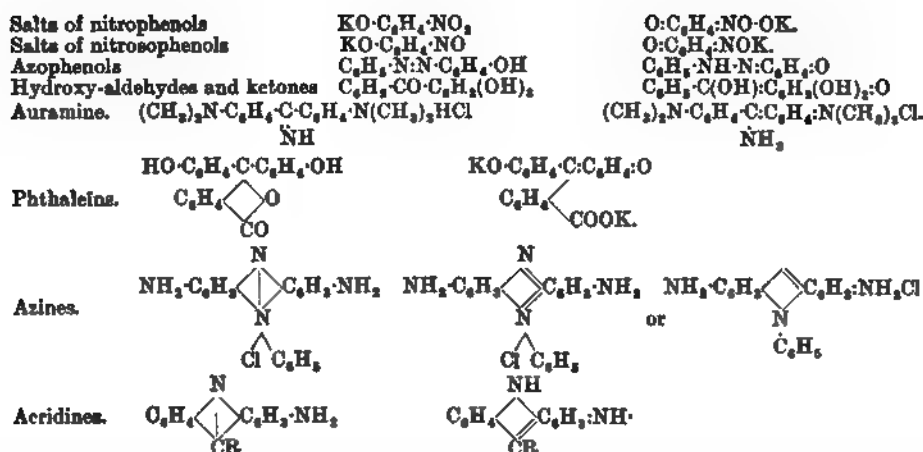$$2:4:6-C_6H_2Br_3.OBr ;$$

is almost certainly to be formulated as

(Thiele and Eichwede, Ber. 1900, 33, 673), for on digestion with lead acetate in acetic acid, 2 : 6-dibromoquinone is produced. It has been suggested that mineral acids and phenols yield oxonium salts derived from the ketonic form (Chem. Soc. Trans. 1904, 85, 1229); e.g.

$$H_2 : C_6H_4 : O<^H_{SO_4H}$$

The homologues of phenol when treated with an excess of halogen, yield products insoluble in alkali (Auwers, Ber. 1895, 28, 2888, 2902, 2910; Zincke, ibid. 3121). To the ' pseudophenols,' the structure of true phenols (I) or of the desmotropic ketones (II)

may be assigned : mere insolubility in alkali is

Salts of nitrophenols $KO\cdot C_6H_4\cdot NO_2$ $O:C_6H_4:NO\cdot OK.$

Salts of nitrosophenols $KO\cdot C_6H_4\cdot NO$ $O:C_6H_4:NOK.$

Azophenols $C_6H_5\cdot N:N\cdot C_6H_4\cdot OH$ $C_6H_5\cdot NH\cdot N:C_6H_4:O$

Hydroxy-aldehydes and ketones $C_6H_5\cdot CO\cdot C_6H_3(OH)_2$ $C_6H_5\cdot C(OH):C_6H_3(OH)_2:O$

Auramine. $(CH_3)_2N\cdot C_6H_4\cdot C\cdot C_6H_4\cdot N(CH_3)_2HCl$ $(CH_3)_2N\cdot C_6H_4\cdot C:C_6H_4:N(CH_3)_2Cl.$

          $\dot{N}H$ $\dot{N}H_2$

Phthaleins.

$HO\cdot C_6H_4\cdot C\cdot C_6H_4\cdot OH$ $KO\cdot C_6H_4\cdot C:C_6H_4:O$

Azines.

Acridines.

assigned to this compound was accepted, but the coloured salts were regarded as quinonoid. The difference of volatility in a current of steam was adduced as an argument favouring a constitutional difference between the isomers; in the light of more recent work, the non-association of the molecules of the ortho- and the association of those of the para- compound (Auwers, Zeitsch. physikal. Chem. 1893, 12, 689; 1894, 15. 33; 1895, 18, 595, and other papers); Hewitt and Winmill (Chem. Soc. Trans. 1907, 91, 441; Thole, *ibid.* 1910, 97, 2596) may account for the difference in the vapour pressures of the two substances at 100°. Armstrong encountered difficulty with *m*-nitraniline; the compound can hardly be quinonoid, it is nevertheless coloured, although the benzoate is colourless.

Meanwhile Hantzsch's work on pseudo-acids had appeared and afforded considerable support to the idea that acids and their salts are frequently constituted in a different manner (Ber. 1899, 32, 575, 607, 628, 641, 3066, 3089, 3101, 3137; 1901, 34, 3430; 1902, 35, 210, 226, 1001, 2724; 1905, 38, 1005, 1013, 1022, 2326, 1906, 39, 139, 162, 1073, 1084, 2098, 2472, 2478, 2703, 3072, 3080, 4153; 40, 330, 1523, 1533, 1556, 4875; 1908, 41 1745; 1909, 42, 966, 986, 1000, 1007; 43, 45, 68, 82, 95, 1685; 1911, 44, 1783). the case of nitroform and its potassium salt, a good case was made out for the respective formulæ (Hantzsch and Rinkenberger, Ber. 1899, 32, 628) $CH(NO_2)_3$ and $C(NO_2)_2(:NO\cdot OK)$.
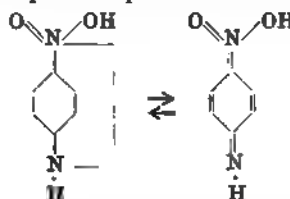
Hantzsch went so far as to state that any colourless hydrogen compound which gives coloured ions is a pseudo-acid; *i.e.*, the free hydrogen compound and its salts possess different constitutions (Ber. 1899, 32, 578).

Other observers have explained anomalous results in the selective absorption or fluorescence of nitro-compounds by assuming the change
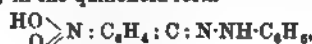
$$X(\cdot NO_2)(\cdot OH) \rightarrow X(:NO\cdot OK)(:O)$$

(Chem. Soc. Trans. 1900, 77, 1324; 1902, 81, 893; 1906, 89, 19), whilst Baly, Edwards and Stewart (Chem. Soc. Trans. 1906, 89, 514) concluded from a comparison of the absorption spectra of *p*-nitrophenol and its sodium salt that 'the residual affinity of the oxygen atoms of
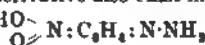
the nitro-group exerts insufficient attraction for the hydrogen of the free nitrophenol to cause the formation of the quinonoid form, but that when the hydrogen is replaced by the more electro-positive sodium atom, then the attraction of the oxygen atom is sufficient to bring the sodium over, with the formation of the quinonoid form.' A similar relationship was assumed in the case of orthonitrophenol and its sodium salt, whilst the yellow colour of *p*-nitroaniline was explained by its molecules existing in quinonoid phases

The transitory existence of a meta-quinonoid linking was also assumed to account for the phenomena observed with *m*-nitroaniline and *m*-nitrophenol. Baly and Tuck subsequently extended their views (Chem. Soc. Trans. 1906, 89, 982), stating that the phenylhydrazones of the three nitrobenzaldehydes exist partly or entirely in the quinonoid form

$$\frac{HO}{O}{>}N:C_6H_4:C:N\cdot NH\cdot C_6H_5,$$

whilst *p*-nitrophenylhydrazine and its acetone derivative also exist in the quinonoid forms

$$\frac{HO}{O}{>}N:C_6H_4:N\cdot NH_2$$

and $\frac{HO}{O}{>}N:C_6H_4:N\cdot N:C(CH_3)_2$

Chemical evidence for the assumed change was lacking until Hantzsch and Gorke (Ber. 1906, 39, 1073) showed that under certain conditions the silver salts of the nitro-phenols yield coloured *aci*-esters on reacting with alkyl halides. These compounds are extremely labile, are readily hydrolysed and undergo spontaneous change into the nearly or quite colourless nitro-aryl-alkyl ethers. Hantzsch states that their colour points to quinonoid structures.

racemic compounds have, as a rule, the greater specific gravity (Liebisch. Annalen. 1895, 256, 140; Walden, Ber. 1896, 29, 1699,.

3. *Solubility and melting-point.* There appears to be a certain relation between the solubility and melting-point on the one hand, and the specific gravities on the other, of the racemic and active forms. If the specific gravity of the racemic compound is greater, the melting-point is higher and it is also less soluble. If the specific gravity is less, the melting-point and solubility are reversed. The following examples exhibit these relationships.

	Sp.gr.		M.p.		Solubility	
Substance	a.	r.	a.	r.	a.	r.
Malic acid .	1·595	1·601	100°	130°–131°	greater	less
Camphoric acid	1·186	1·229	187°	205°–206°	greater	less
Tartaric acid .	1·754	1·697	170°	204°	greater	less
Mandelic acid	1·341	1·300	130°	118°–119°	less	greater

4. *Absorption spectra.* These have been shown by Stewart to be different in the active and racemic forms.

5. *Water of crystallisation.* It is a common observation that the active and racemic forms usually contain different amounts of water of crystallisation.

Substance	a.	r.
Tartaric acid . . .	—	H_2O
Ammonium tartrate .	—	$2H_2O$
Potassium ,, .	$\tfrac{1}{2}H_2O$	$2H_2O$
Thallium ,, .	$\tfrac{1}{2}H_2O$	—
Sodium ,, .	$2H_2O$	$2H_2O$
Potassium lithium tartrate	H_2O	H_2O
Potassium antimonyl ,. .	$\tfrac{1}{2}H_2O$	$\tfrac{1}{2}H_2O$
Strontium glycerate .	$3H_2O$	$\tfrac{1}{2}H_2O$
Barium ,. .	$2H_2O$	$\tfrac{1}{2}H_2O$
Calcium galactonate .	$5H_2O$	$2\tfrac{1}{2}H_2O$
Barium ,, .	$5H_2O(?)$	$2\tfrac{1}{4}H_2O$

6. *Physiological properties.* Chabrié has shown that racemic acid is less poisonous than the active tartaric acids, and Tiemann and Schmidt noticed that inactive terpenes often have a fainter odour than the active forms.

In dilute solution the racemic compound dissociates into its two active components and consequently the solution behaves like a mixture of the two enantiomorphs. It has no action on polarised light, and such properties as vapour pressure, specific gravity, magnetic rotation and electrical conductivity (in the case of an acid) are identical with those of a mixture of the active components. The vapour density is also the same. Thus, Anschütz (Ber. 1885, 18, 1397) has shown that ethyl racemate is mono-molecular when vapourised.

Methods of distinguishing racemic compounds from mixtures. The criteria for determining whether an inactive, crystalline substance is (1) a mixture or *conglomerate* of equal quantities of the two kinds of crystals not forming a compound; (2) a true *racemic compound*, that is, a compound consisting of equal molecules of the two enantiomorphs; or (3) an isomorphous mixture or mixed crystal (called also a *pseudo-acemic compound*), have been examined by Bakhuis Roozeboom (Zeitsch. physikal. Chem. 1899, 28, 494) from the standpoint of the phase rule, and he has shown that the melting-point and solubility afford the most trustworthy evidence of racemism.

Melting-point of conglomerates. In this case

each enantiomorph must be regarded as a separate individual and the melting-point of each (when present in excess, it may be regarded as the solvent), will be lowered by the addition of the second enantiomorph, the eutectic or mixture of minimum melting-point being reached when both are present in equal quantity. The melting-point curves of the two enantiomorphs will have the following form :—
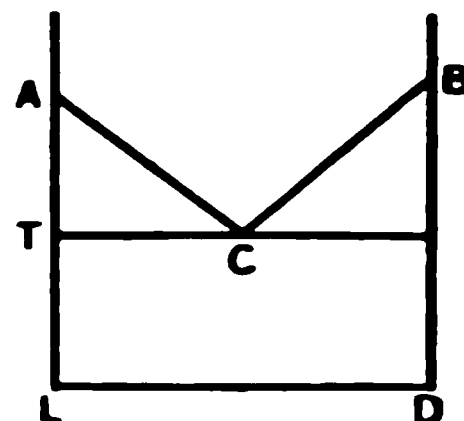

Fig. 1.

If A and B represent the melting-point of the pure lævo- and dextro-enantiomorphs (L and D), AC and CB will represent the melting-point curves of each of the enantiomorphs when mixed with increasing proportions of the other, and C the melting-point of the inactive mixture when equal quantities of the two are present. Consequently when either enantiomorph is added to the conglomerate the melting-point will be raised.

Melting-point of racemic compounds. The melting-point curve of a racemic compound and its two enantiomorphs will form three curves, for there are three individuals, and according to whether the racemic compound has a higher or lower melting-point than the enantiomorphs the curves will take the following forms.
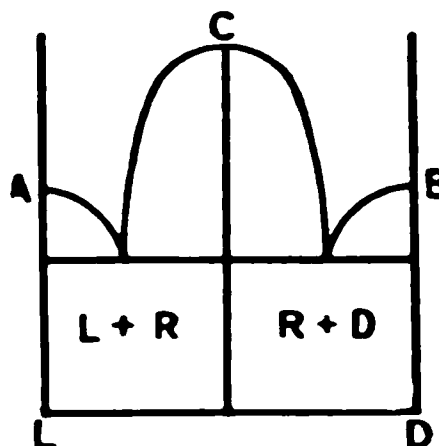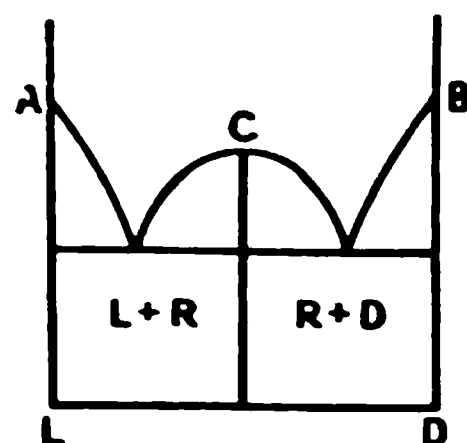

Fig. 2.　　　　　Fig. 3.

Thus active dimethyl tartrate melts at 43·3° ; racemic dimethyl tartrate at 89·4°, and the curve would take form represented in Fig. 2, whilst active mandelic acid melts at 132·8° and the racemic acid at 118° and would have the form shown in Fig. 3. Here the addition of a small amount of either enantiomorph to the racemic compound will lower the melting-point.

Melting-point of pseudoracemic mixed crystals. If the two enantiomorphs are isomorphous and form mixed crystals they form only a single phase and the fusion-point will depend upon the composition of the solid which separates from the fused mass. If it is identical with that of the fused mass, a constant melting-point for any mixture is obtained. This has been observed in the case of the two active camphoroximes. The curve is then a horizontal line

joining the melting-points of the enantiomorphs, Fig. 4.

This property is exhibited by 1-amyl-3-nitrophthalates; the compounds themselves and mixtures melt at 116°, also by 2-amyl-3-nitro-
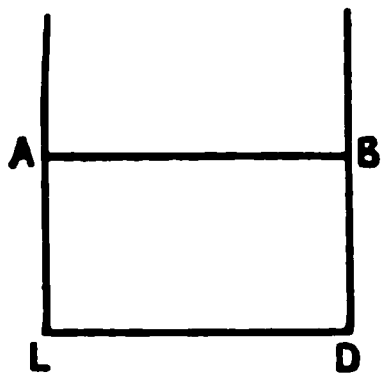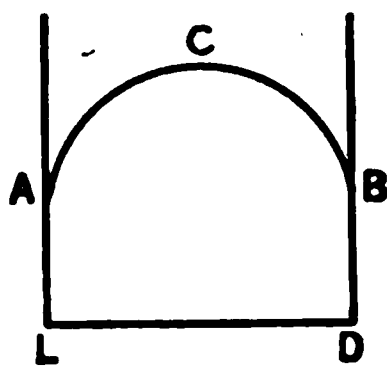

FIG. 4. FIG. 5.

phthalates which melt at 155°, and amyl phenylcarbamates which melt at 31° (W. Marckwald and Nolda, Ber. 1909, 42, 1583).

If, on the other hand, the solid which separates differs in composition from the fused mass, the melting-point curve will be either convex or concave. The former, Fig. 5, will occur when the concentration of the second enantiomorph in the separated solid is less, the latter, Fig. 6, when it is greater than in the
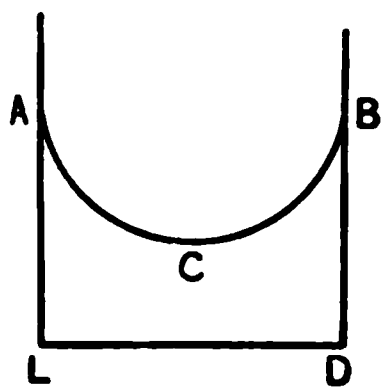

FIG. 6.

fused mass. The curve in both cases will be a continuous one and reach its maximum or minimum at c when equal quantities of both enantiomorphs are present. A maximum, 91·4°, has been observed in the case of the carvoximes, the enantiomorphs melting at 72°; and a minimum in that of d- and dl-amyl carbamates (W. Marckwald and Nolda, Ber. 1909, 42, 1583).

The above criteria in regard to the nature of an inactive substance only hold in the neighbourhood of the melting-points. At other temperatures, transformations may occur of a racemic compound to a pseudoracemic compound or a conglomerate or vice versa.

Solubilities of racemic compounds and mixtures. The phase rule may also be applied to the equilibrium between a racemic compound or mixture and its saturated solution in precisely the same way as to a mixed and double salt. A system consisting of a mixture of the dextro- and lævo- enantiomorphs in equilibrium with a saturated solution is a 3-component system and is invariant for a given temperature. The isothermal solubility curve of each will vary (increase or decrease) with each addition of the other enantiomorph until a maximum or minimum solubility point is reached when both are present in equal quantity, that is, when an inactive mixture is formed. If either enantiomorph is now added no change will result, for the solution is saturated in regard to each enantiomorph and neither will be dissolved. In

Fig. 7, if the vertical represents the concentration of the lævo and the horizontal that of the dextro enantiomorph, the upper solubility curve acb represents that of a mixture (above or below the transition point of the racemic compound). The point c will lie on the line OB equidistant between the horizontal and vertical, since the two enantiomorphs possess identical solubilities. The solubility curve for the pure racemic compound will also cut the line OB either above or below c, depending on the transition temperature and, as in the former case, the point will be a maximum or minimum according to whether the solubility of the racemic compound increases or decreases in presence of excess of either enantiomorph.
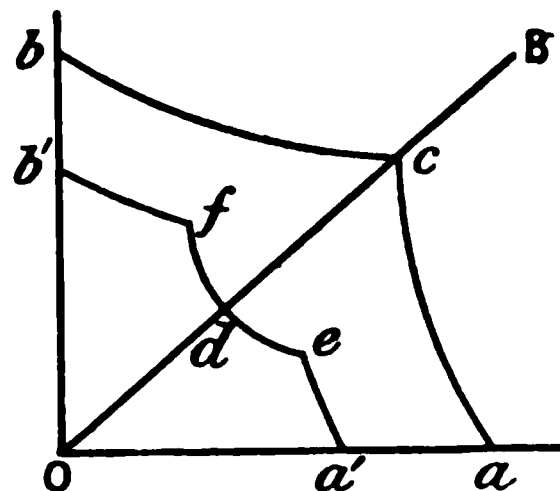

FIG. 7.

The curve a'efb', in Fig. 7, represents the solubility curve for rubidium racemate, the transition point of which lies below that of the conglomerate. The addition of an excess of either enantiomorph will introduce a new phase and a new equilibrium will be established which will lie on df or de according to the enantimorph added; in other words, the solubility will be different from that of the pure racemic compound, and moreover some of the active component will pass into solution. Thus, by comparing the concentrations of the saturated solutions before and after addition of the enantiomorph, it would be possible to ascertain whether the original substance were a racemic compound or a conglomerate. Moreover, the addition of either enantiomorph to the solution of the racemic compound would produce an optically active solution which could be readily observed in the polarimeter. These facts have been demonstrated experimentally by Kendrick (Ber. 1897, 30, 1749) in the case of r-ammonium bimalate.

Partial racemism. The term is applied to those cases in which a double salt is formed, consisting of equal molecules of two active components which are not enantiomorphs. The phenomenon was first observed by Pasteur, who obtained crystals of a double salt of ammonium d-tartrate and ammonium l-malate. Another form of combination to which Ladenburg first applied the term partially racemic compound was observed by him in the case of quinine pyrotartrate, which forms three series of salts, from one of which the d-acid, from a second the l-acid, and from a third the inactive acid was separated. The quinine in the third case must therefore have united with the unresolved racemic acid or, what amounts to the same thing, a double salt of quinine d- and l-tartrate must have been formed.

is always at a temperature above surrounding bodies (Compt. rend. 1904, 136). Many experimenters have since measured the heat emitted by radium, and the latest determination by Schweidler and Hess gives the value 118

Actinium Series.

Radiation	Period	Product	Radiation
α(4·55 cm.)β		Actinium	α(2·58 cm.)
α(4·17 cm.)	10·5 days	Radio Ao	β and γ
α(5·40 cm.)	10·5 days	AcX	α(3·67 cm.)β
α(6·10 cm.)	3·9 secs.	Ac emanation	α(5·7 om.)β
α	0·002 sec.	AcA	α(5·5 cm.)
α β	36 mins.	AcB	α
α(5·12 cm.)	2·15 mins.	AcC	β
α	4·71 mins.	AcD	α(5·0 om.)
			α(8·6 cm.)
			β

Thorium Series.

Period	Product	Radiation
3×10⁹ years	Thorium	α(2·58 cm.)
5·5 years	Meso Th₁	β and γ
6·2 hours	Meso Th₂	β(α?)
737 days	Radio Th	α(2·84 cm.)
3·7 days	ThX	α(3·13 cm.)β
53 secs.	Th emanation	α(3·94 cm.)
0·14 sec.	ThA	α(4·50 cm.)
10·6 hours	ThB	β and γ
55 mins.	ThC₁	α(6·57 cm.)
?	ThC₂	β
3·1 mins.	ThD	β
		β

Uranium Series.

Product	Period	Radiation
Uranium	6×10⁹ years	α(2·58 cm.)
UrX	24·6 days	β and γ
(UrY)	1·5 days	β(α?)
Ionium	2×10⁶ years	α(2·84 cm.)
Radium	2000 years	α(3·13 cm.)β
Ra emanation	3·85 days	α(3·94 cm.)
RaA	3 mins.	α(4·50 cm.)
RaB	26·7 mins.	β and γ
RaC₁	19·5 mins.	α(6·57 cm.)
(RaC₂)	1·4 min.	β
RaD	16·5 years	β
RaE	5 days	α(3·58 cm.)
RaF (Polonium)	140 days	
Lead?		

calories per hour per gram of radium (Wien. Ber. 1908). Rutherford and Barnes have made a detailed examination of the heat emitted by the products of radium separately, and have shown that the heat generated is derived from

the energy of the α particles emitted (Phil. Mag. 1904). The β and γ rays seem to be responsible only for a very small part of the heat evolved. Measurements on other products have confirmed the view that the heat developed in radio-active changes is proportional to the energy of the α particles. It will be noticed that the emission of heat by radium is very large, being sufficient to melt its own weight of ice in 40 minutes. This evolution of energy during radio-active changes may be taken as indicative of the enormous stores of energy which must be contained within the atoms.

The figures in this table show a certain relation between the period p of a substance emitting α rays, and the range r of those rays. Rutherford was the first to draw attention to the existence of such a relation, pointing out that in general p was large when r was small (Phil. Mag. 1907). Geiger and Nuttall have made fresh determinations of several ranges which had previously been somewhat uncertain; these have been used in the construction of the table (ibid., 1911). They have taken the opportunity to re-examine the relation between p and r and find that for the radium series, and also for the actinium series, p and r are connected by the relation $rp^a = b$. Here a and b are constants, the former being the same for both series. The figures for the thorium series have not yet been completed. If the relation can be relied on, a very interesting result appears. It can be shown that the life of a substance emitting rays of short range, say 1 cm. would be so long, and therefore its transformation so slow, that its activity would be beyond the limits of detection by present methods. W. M.

II. This section deals with the phenomena attending the passage of α-, β-, and γ-rays through matter.

It is convenient to divide them into two parts : (i.) those referring to the action upon the rays; (ii.) those referring to the action upon the matter.

Further subdivision is convenient in respect to the phenomena of part (i.). The experience of an α-, a β-, or a γ-ray as it flies across an atom may be considered under three heads : (a) loss of energy, (b) deflection, (c) transformation or replacement. The α particle's experiences are mostly under (a) : it is only slightly liable to scattering (b), and not at all to change of form (c). The β particle is very liable to deflection, which often makes its loss of energy difficult to detect, and it is liable to transformation into a γ-ray— the X-ray may be included as a form of γ-ray— especially if its velocity is not more than about one-third of that of light. The γ-ray (or X-ray) appears to suffer no loss of energy, and is somewhat liable to scattering; the most interesting and important event in its history is the transformation of its energy into that of a β-ray.

The most obvious of the phenomena to be included under (ii.) are heating, photographic action, phosphorescence, ionisation. The last three are used as indicators of the action of the rays.

General considerations.—In all cases known the phenomena of part (i.) are independent of physical and chemical conditions. For example, the probable loss of energy of an α particle in

going through a definite small volume containing an atom does not depend on whether the atom is part of a hot body or of a cold body, of a solid or of a gas, of a simple molecule or of a complex one.

On the other hand, some of the phenomena of part (ii.) are not quite so simple. The number of ions which can be extracted from a gas after an α-particle has passed through it depends somewhat upon molecular association.

The α- and β-rays are really projectiles of very small mass, but of enormous speed. It would appear that the γ-ray (and the X-ray which has similar properties) may also be reasonably and usefully considered as a projectile. In the case of any of these forms of radiation small entities, quanta, or corpuscles are hurled against matter with relative speeds far exceeding those of the thermal agitation of a gas at any temperature yet realised. The results are peculiar, as might be expected. In particular the atoms are no longer impenetrable, but are traversed with the utmost freedom; and the actions and reactions between the projectiles and the atoms are of the greatest interest, affording glimpses of the atomic constitution from an entirely new standpoint.

We now take the three radiations in turn.

The α-ray.—The almost universal presence of helium in radioactive minerals early suggested the nature of the α-particle. A simple verification has been given by Rutherford and Royds (Phil. Mag. 1909). Radium emanation is enclosed in a glass tube with very thin walls, through which α radiation can pass. Outside the tube is an evacuated space, which shows no trace of the helium spectrum when sparked through immediately after the preparation of the tube. In a few days, however, the helium lines are strongly shown. In control experiments, when the inner tube is empty, and even when it is filled with helium, there is no such effect. It is clear that the emanation has shot helium through the glass.

Rutherford has determined the velocity of the α particle and the ratio of its charge to its mass by observing the effect of electric and magnetic fields upon its flight (Phil. Mag. 1906). The latter quantity he finds to be nearly 5×10^3, which shows that the α particle being a helium atom must carry twice the unit charge. The velocity will be considered later.

Since the α particle is very little scattered by the matter through which it passes, its path is almost exactly a straight line. It spends its energy as it goes, and, having spent it, comes to comparative rest at a certain distance from the starting-point, which distance is called the range. The range varies with the initial speed and with the nature and density of the gas traversed. It was first found, in the case of the α-rays of radium, by means of apparatus represented in the diagram (Fig. 1). A very thin layer of radium is placed on a plate RR. The α-rays stream upwards in all directions, but only those which proceed almost vertically succeed in passing through the set of tubes, TT. These are made of thin copper foil 1 cm. long and 2 mm. wide; the bundle contains about 150 of them. The α-rays which strike the walls of the tubes are embedded there. The rest stream upwards, ionising the gas; if they reach

the gauze BB, and enter the ionisation chamber between BB and AA, then ionisation occurs in the chamber also, and is detected in the usual way. The lower gauze, CC, is connected with
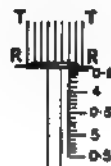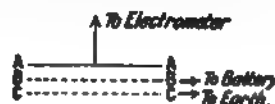

Fig. 1.

the earth, and the field between BB and CC protects the ionisation chamber from the intrusion of ions from below. The radium is gradually raised towards the chamber and the current measured for different positions; the 'ionisation curve' is thus obtained (Fig. 2) (Bragg and Kleeman, Phil. Mag. 1905). This curve is interpreted as follows. The small readings above A are due to the action of β- and γ-rays.

Fig. 2.

The sudden setting in of current at A, 7·14 cm. from the origin, implies that this is the furthest point of penetration of the α-rays. This distance is termed the range of the α particle in question. It is 7·14 cm. in air at a pressure of 76 cm. and a temperature of 20°. The range at any other pressure (P) and absolute temperature (T) is $7 \cdot 14 \times (76/P) \times (T/293)$. The slope, AB, is due to the fact that all the α-rays do not reach quite the same distance from the radium; the turn at B shows that at 6·5 cm. all the rays—of this stream—now make their way into the chamber. The gradual bend back, BC, implies that the α-particle is more effective as an ioniser as it slows down. The sudden break out again at C (4·84 cm.), shows that the chamber is now

proportion that are converted into β-rays in crossing a given stratum of that substance. If this proportion is put equal to λdr, where dr is the product of the thickness of the stratum and its density, then for most substances λ is nearly 0·040 in the case of the γ-rays of radium and 0·017 in the case of the γ-rays of uranium. For lead and other substances of high atomic weight, it is a little larger, for example, Soddy and Russell, Phil. Mag. 1910).

The scattering of the γ-ray in its passage through matter has been examined by several workers, e.g., Madsen (Trans. Roy. Soc. of South Australia, 1908) and Florance (Phil. Mag. 1910). The latter states that if a stream of heterogeneous γ-rays from radium is scattered in passing through matter, that which is less penetrating is more scattered than that which is more penetrating. The analogous effect occurs in the case of the β-rays.

The nature of the γ-ray is still a matter of discussion. The æther pulse theory supposes the γ-ray to be the disturbance in the æther which must occur when a β-ray is discharged from the atom. Such a supposition links closely together γ-rays, X-rays, and light as variants of one form of radiation, and is based on the many points of resemblance between the three. Amongst resemblances of especial interest may be mentioned Barkla's discovery that X-rays can be polarised in a manner suggestive in some degree of the polarisation of light, and the remarkable experiments of Friedrich, Knipping, and Lane, which are best explained on the supposition that X-rays can be reflected in such planes within a crystal as are rich in atoms. The pulse theory is, however, unable to give a ready explanation of the interchangeability of X-ray and β-ray energy.

If the ionisation in a gas traversed by γ-rays is due to the β-rays produced by the γ-rays in the walls and in the gas, the 'ionisation of gases by γ-rays' is really an ionisation by β-rays. In the fourth column of Table II. some of the values found for the ionisation of gases by γ-rays are set out, and may be compared with the values in the third column (Kleeman, Proc. Roy. Soc. 79, 231).

W. H. B.

RADISH, Raphanus sativus (Linn.). Several varieties have been distinguished, e.g. R. s. griseus, R. s. radicula, and R. s. tristis. The first produces seeds rich in oil, the second yields very small edible tap roots, whilst the third is valued for its relatively large tap root. The roots of all possess the well-known pungent flavour due to allyl iso-thiocyanate. König gives, as the composition of the edible portions of the roots—

	Water	Protein	Fat	Sugar	Other N-free ext.	Crude fibre	Ash
R. s. tristis	86·9	1·9	0·1	1·5	6·9	1·6	1·1
R. s. radicula	93·0	1·2	0·2	0·9	2·9	0·8	0·7

According to Saiki (Zeitsch. physiol. Chem. 1906, 48, 469), radishes contain a powerful diastatic ferment, which can be obtained in the form of a yellowish-white, somewhat hygroscopic powder. Little or no starch is present in the root under normal conditions, but when the plants are watered with a solution containing from 4 to 10 grms. of sodium chloride per litre, the

roots contain considerable quantities of starch (Lesage, Compt. rend. 1891, 113, 373). Boric acid has been found in radishes (Gessend, Ann. Agron. 1891, 17, 352. By distilling an aqueous extract of Raphanus niger (Mill.) (R. sativus, Moreigne (J. Pharm. Chim. 1896, 4, 10) obtained a crystalline substance, raphanol $C_{20}H_{34}O_6$, melting at 62° and soluble in ether, chloroform, benzene, or light petroleum.

According to Kellner (Landw. Versuchs. Stat. 1883, 30, 42, a gigantic variety of radish, single roots of which attain a weight of 2½ to 3 kilos, is much esteemed as a vegetable in Japan. He found this to contain—

Water	Protein	Fat	Soluble carbohydrates	Crude fibre	Ash
93·45	0·67	0·07	4·40	0·77	0·43

about two-thirds of the total nitrogen being present as real proteids. The ash contained—

K_2O	Na_2O	MgO	CaO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
46·4	2·4	4·7	9·4	0·6	10·1	13·1	2·6	11·9

The proportion of sulphur, in organic combination, in the roots, varies from 0·22 to 0·07 p.c.

Another Japanese species, R. caudatus (Linn.), is valued for its seed pods, which are about twice the size of those of the common radish, and are eaten as a salad or pickled in vinegar (Rep. New York Expt. Stat. 1884). According to Sacher (Chem. Zeit. 1910, 34, 1192 and 1333), the skins of the red radish, extracted for a few hours with their own weight of 90 p.c. alcohol, yield a solution which serves as a delicate and useful indicator for acids and alkalis, turning intensely red with the former and green with the latter.

H. I.

RADIUM. Symbol Ra. At.wt. 226. A radioactive element discovered by M. and Mme. Curie in the pitchblende from Joachimsthal (P. Curie, S. Curie and G. Bémont, Compt. rend. 1898, 127, 1215).

Occurrence. All ores containing uranium also contain radium. In the majority of them, the ratio of radium to uranium is equal to the 'equilibrium ratio' $3·2 \times 10^{-7}$, i.e. 320 mgm. radium are present per ton of uranium (c. McCoy, Ber. 1904, 37, 2641). In autunite, a hydrated calcium uranium phosphate which occurs in France and Portugal, the proportion of radium is only from 20 to 80 p.c. of the above, radioactive equilibrium not having been established. Geologically, old formations contain a slightly larger radium ratio than the more recent formations (Mlle. Gleditsch, Le Radium, 1911, 8, 256).

The extremely delicate emanation test for radium reveals the presence of that element in all common rocks and minerals, and in natural springs, both hot and cold. Most of the celebrated spas contain appreciable quantities of radium or its emanation.

Radium preparations are usually prepared from pitchblende, an impure uranosouranic oxide, occurring in Cornwall, in Bohemia (Joachimsthal), &c.

Extraction from pitchblende. The crushed mineral, after a preliminary roasting in air, is heated with sodium carbonate in a reverberatory furnace. The product is washed with water and then with dilute sulphuric acid, to remove the uranium as soluble uranyl sulphate. All the radium is left in the insoluble residue, which consists mainly of lead and calcium sulphates,

Order	Genus	Species	Occurrence, etc.
Euphorbiaceæ	Hevea	brasiliensis (Muell. Arg.)	*South America*, particularly *Brazil*; employed practically to exclusion of all other trees on Eastern plantations. Forms *Para* rubber of commerce.
„	Manihot	Glaziovii (Muell. Arg.); dichotoma	*Ceará* (*Brazil*); planted to some extent in Africa and tropical America. Forms the *Ceara* or *Manicoba* rubber of commerce.
„	Sapium	Tolimense; verum, &c.	*Central and South America* (*Colombia Virgen*; *Carthagena Scraps*, &c. of commerce).
Apocynaceæ	Funtumia	elastica (Stapf)	*Tropical Africa*; forms *Gold Coast Lumps*, *Ivory Coast Lumps*, and various '*niggers*,' &c. of commerce. Planted in some parts of Africa.
„	Landolphia	owariensis (Beauv.); Heudelotii D.C. Thollonii (Dew.); sphaerocarpa (Jumelle); Pierrei	Creepers occurring in enormous quantities in *Tropical Africa*, forming many of the 'Congo' varieties, '*Madagascars*,' &c. of commerce.
„	Clitandra	Numbers of species of this genus are distributed in many parts of *tropical Africa*, principally Gold Coast and Congo	
„	Hancornia	speciosa (Gomez) (Muell. Arg.)	*Brazil* (Bolivia and Pernambuco) yields the '*Mangabeira*,' *Bahia*, and *Matto-grosso sheets* of commerce.
„	Dyera	costulata (Hook. *f.*)	*Malay Peninsula*; yields '*Jelutong*' of commerce.
Urticaceæ	Ficus	elastica (Roxb.)	*Asia* (Burmah, Malaya, Java, India). Yields the '*Rambong*' of commerce. Has been planted to some extent in the Dutch and German colonies.
„	Castilloa	elastica (Cerv.); *Ulei* (Warb.)	*Mexico*; *Central America*; *Peru*. Planted to some extent in Mexico and German colonies, &c. Yield the '*Caucho*,' '*Mexican strips*,' '*Centrals*,' &c. of commerce.
Compositæ	Parthenium	argentatum (A. Gray)	*Mexico*; *Texas* (*Guayule* of commerce).

coagulating vessels is compressed (*unsmoked*) into irregular masses, and goes by the name of *Negro-heads*. The Amazon territory at the present time supplies about one-half of the world's total output.

Plantation rubber. The tree which has been almost universally adopted on the eastern plantations (Malaya, Ceylon, S. India, Java, Sumatra, Borneo) is the *Hevea brasiliensis*, but the methods of collection and coagulation, &c., are markedly different from those employed on the Amazon. The trees are tapped mostly on the (half) herringbone system, which consists of a series of oblique cuts running into a central channel. The latex is collected in a cup connected with the central channel at the base of the tree. Tappings take place daily or on alternate days over certain periods, the tapping consisting in a paring away of a strip of bark of about 1⁄20th to 1⁄30th of an inch wide along each oblique incision. This is repeated until a certain area of bark has been

removed. The portion of the tree so operated on is then allowed a period of rest sufficient for bark renewal, for which 3 to 4 years appears to be an appropriate period. Plantation latex is generally coagulated by the addition of a small quantity of acetic acid. After the coagulum is formed it is removed from the serum and passed through washing rolls, which squeeze out much of the remanent mother liquor and wash out the excess of non-rubber latex constituents. These rolls are of much the same construction as those used in the factory for *washing* (*see* below). The rubber is subsequently hung up to dry in the form of a sheet or crepe, and is frequently 'smoked' during the drying period, coco-nut husks and hard wood being employed for this purpose. Plantation rubber is invariably shipped bone-dry and is of a translucent light cream to amber colour for ordinary varieties to a dark amber in the case of the smoked goods. Dryness and cleanliness are the characteristics of plantation rubber.

from time immemorial have possessed the resin lac, and were long accustomed to use it for sealing manuscripts before it was known in Europe. It was first imported from the East into Venice, and then into Spain; in which country sealing-wax became the object of a considerable commerce, under the name of Spanish wax. In mediæval times the composition contained bees-wax.

If shellac be compounded into sealing-wax immediately after it has been separated by fusion from the palest qualities of stick or seed lac, it then forms a better and less brittle article than when the shellac is fused a second time. Hence sealing-wax rightly prepared in the East Indies deserves a preference over that made in other countries, where the lac is not indigenous. Shellac can be restored in some degree, however, to a plastic and tenacious state by melting it with a very small portion of turpentine. The palest shellac is to be selected for bright-coloured sealing-wax, the dark kind being reserved for black.

The following proportions may be followed for making red sealing-wax. Take 7 oz. of shellac, 4 oz. of Venetian turpentine, and 3–4 oz. of vermilion. Melt the lac in a copper pan suspended over a clear fire, then pour the turpentine slowly into it, and soon afterwards add the vermilion, stirring the mixture briskly all the time with a rod in either hand. In forming the round sticks of sealing-wax, a certain portion of the mass should be weighed while it is ductile, divided into the desired number of pieces, and then rolled out upon a warm marble slab, by means of a smooth wooden block, like that used in apothecaries for rolling a mass of pills. The oval sticks of sealing-wax are cast in moulds, which are

are in general use, the volume and nature of the trade waste, the amount of dilution by subsoil or surface water, &c.

Failing satisfactory evidence to the contrary, it will be desirable to assume that the sewage is 'strong' for the purpose of estimating the required capacity for the disposal works.

For the purpose of showing the *minimum* total cubic contents of filters required for treating three times the dry weather flow in different cases, the tables A and B have been prepared on the data given in the Commission's Report. Wherever possible, the figures are calculated from the data on pp. 117 and 118 of the Fifth Report, otherwise the calculations are based on the data in the tables between pp. 202 and 203.

The rates of filtration given by the Commission are rates which can generally be *doubled* in wet weather. Where it is proposed to deal with *three* times the dry-weather flow, the Commission say that it would generally only be necessary to provide 1½ times the capacity of filter required for the dry-weather flow (paragraph 293 of Report, 209). Hence the rates of filtration given by the Commission must be reduced by one-third to arrive at the basis for calculating the size of the filters for *three* times the dry-weather flow, and this reduction has been made in arriving at the figures in the tables.

TABLE A.—CONSTANTS FOR CALCULATING THE MINIMUM CUBICAL CONTENTS OF PERCOLATING FILTERS.

Preliminary treatment	Strong sewage		Sewage of average strength		Weak sewage	
	Coarse or medium material	Fine material	Coarse or medium material	Fine material	Coarse or medium material	Fine material
Detritus tanks	15	*	25	*	40	*
Septic tanks	45 †	*	70	*	100	100
Settlement tanks (continuous flow) .	45 †	*	70	*	100	100
„ „ (quiescent) . .	50 †	25	100	70	130	130
Precipitation tanks (continuous flow)	65	50	100	80	150	175
„ „ (quiescent) .	100	65	130	130	170	200

Notes as to filtering material. (a) A filter may be regarded as 'coarse' if the material will not pass through a 1-inch sieve; as 'medium' if it will pass through a 1-inch but not through a ½-inch sieve; and as 'fine' if it will pass through a ¼-inch sieve.

(b) 'Coarse' material will be desirable in all cases where the liquid to be treated contains much suspended matter.

(c) In the cases marked *, the use of fine material would not be desirable unless the circumstances were exceptional.

If 'medium' sized material were used in the cases marked †, the figures should be reduced by about 10.

TABLE B.—CONSTANTS FOR CALCULATING THE MINIMUM CUBICAL CONTENTS OF CONTACT BEDS.

Preliminary treatment	Strong sewage			Sewage of average strength			Weak sewage		
	Single contact	Double contact	Triple contact	Single contact	Double contact	Triple contact	Single contact	Double contact	Triple contact
Detritus tanks	—	—	25 *	—	25	†	—	38	†
Septic tanks	—	—	33	—	38	†	75 *	66 ‡	†
Settlement tanks (continuous flow)	—	—	33	—	38	†	75 *	66 ‡	†
„ „ (quiescent) . .	—	—	44	—	50	†	100	†	†
Precipitation tanks (continuous flow)	—	33	†	—	50	†	133 ‡	†	†
„ „ (quiescent) .	—	43	†	—	66 *	†	133 ‡	†	†

Notes. (a) The beds should not be less than 2 ft. 6 ins. nor more than 6 ft. in depth.

(b) The different series of beds, in double and triple contacts, should have equal cubic contents, failing any evidence to the contrary.

(c) Where a blank is left in the tables, the particular treatment indicated would only be desirable in exceptional circumstances, as the method would not generally be economical.

(d) In the cases marked thus †, the particular treatment indicated would only be necessary in exceptional circumstances (i.e. when an unusually good effluent is required).

(e) Where three times the d.w.f. has to be

dealt with in wet weather, the individual beds, in the cases marked ‡, should be small (to facilitate rapid filling and emptying) or the total cubic contents of the filters should be increased.

(f) The average liquid capacity of a cubic yard of contact bed is about 50 gallons. There are no data in the Commissioners' report with regard to the cases marked thus *.

In order to ascertain the minimum total cubic contents of the filters required, divide the dry-weather flow by the *appropriate figure* (having regard to the strength of the sewage and the kind of treatment proposed) in the tables and the result will be the number of cubic yards

the canvas, and after a time is removed by a bath of dilute hydrochloric acid.

The silver is precipitated from the clear solutions either by zinc-dust or zinc shavings. Zinc dust is mixed with the solution in tanks and separated by filter pressing, but zinc shavings are contained in boxes through which the solution is allowed to flow. The solutions are less dilute in cyanide than those used for gold ores, and contain large quantities of silver, and

Fig. 3.

owing to these facts coarse zinc shavings are used, not coated with lead. The zinc-silver couple, soon formed by precipitation of the silver, gives a high precipitating efficiency to the zinc and enables the lead-zinc couple to be dispensed with.

In recovering the silver from the zinc boxes, simple screening of the precipitate separates the zinc and gives a product containing 50–70 p.c. of silver, which is briquetted by air pressure, partly dried, and smelted with 2 p.c. of nitre without any treatment with acid or by roasting.

Fig. 4.

Large (No. 300) graphite pots or steel pots are used. The silver thus produced is somewhat impure and is sometimes refined by passing air through the molten bullion, as proposed by Rose (see Min. Ind. 1910, 320).

The cyanide consumption on Mexican silver ores varies from 1 to 4 lbs. per ton, and 70–90 p.c. of the silver is recovered. Although power in Mexico is cheap (30s. per H.P. per month for transmitted electric power) and unskilled peon labour is only 1s. 6d. per day, the cost of treatment, according to Caldecott, is heavy,

Aerial tramway bucket bringing ore from mine

↓

9 Grizzleys : each 12′ × 4′, 1½″ space

↓

Bigelow breakers

↓

Ore bin to hold 1900 tons

↓

Pepler feeders

Cyanide solution ↘ ↓

Stamp battery, 36 head, each 1250 lbs.

↓

3 Callow screens, 'Simplex'

↙

3 Hydraulic sizers, 3′ 6″ → 3 hydraulic sizers, 5′ 6″

↓ ↓

3 Wilfley tables, coarse sand   9 Wilfley tables, fine sand

↙   ↘   ↓   ↘

concentrate   3 Dorr separators, double ←   concentrate

↘↖

6 Tube mills, 52″ × 16′

3 Dorr thickeners, 30′ × 10′

↓   ↘

30 Johnston's slime concentrators   Solution, to stamp battery

↙   ↓

concentrate   Pumps

↓

3 Dorr thickeners, 30′ × 10′

↙   ↘

Solution, to stamp battery   6 Brown agitators, 45′ × 15′

↓

2 Cyanippus decantors, 45′ × 15′

| ↓

↓   Dehne clarifiers

5 Merrill slime presses   ↙

↙   ↘   ↙

Residue, to waste   Precipitating plant (by zinc dust)

↓

3 Merrill precipitation presses

↓

3 Tilting furnaces

↓

Bullion

Fatty acids (*see* OILS, FIXED, AND FATS). These soaps are prepared by double decomposition of the alkali soaps with aqueous solutions of salts of the alkaline earths or metals, or by heating the free fatty acids with the oxides or carbonates of the metals.

These soaps are employed in the arts for the most varied purposes, extensive use being made of their property of dissolving, to a considerable extent, in petroleum ether, naphtha, heavier petroleum hydrocarbons, coal-tar oils (carbolic acid), oil of turpentine, and fatty oils. Their solubility is increased by the presence of free fatty acids.

The most important soaps are—

Lead soaps (lead plaster) consisting chiefly of lead oleate.

Magnesium oleate, used in the process of dry-cleaning to prevent spontaneous ignition. **Aluminium soaps** enter into many compositions for waterproofing textile goods and papers, for preparing substitutes for leather, celluloid, india-rubber substitutes for insulating purposes, &c. Aluminium oleate is used especially as an 'oil thickener.' **Lead and manganese soaps** are used as 'driers' (*q.v.*) in the manufacture of boiled oils and varnishes. **Zinc, iron, nickel, cobalt, and chromium soaps** are employed in the manufacture of coloured varnishes, as also for waterproofing leather and canvas, and to some extent as 'driers.' **Copper and mercury soaps** serve in the production of anti-fouling preparations, especially in the manufacture of paints for ship bottoms.

In this class of soaps must be also included the *metallic rosinates*, chiefly used as 'driers' (*q.v.*).

In the analytical examination the water-insoluble soaps are decomposed by means of a suitable mineral acid (hydrochloric, nitric, sulphuric), when the fatty acids are obtained as an oily layer; or, if the salts be decomposed under ether (which in many cases is the most advisable course), in ethereal solution, and the metal passes into the acid solution. Both the fatty acids and the acid liquor are then examined in the usual manner. J. L.

SOAP-BARK and **SOAP-ROOT.** Soap-bark is the bark of a Chilean rosaceous tree, *Quillaja saponaria* (Mol.). The thin black dead bark has usually been almost or entirely removed from the commercial product, which consists mainly or exclusively of the heavy white layer of bast which glitters with crystals of calcium oxalate. This salt is mainly responsible for the large amount (13 p.c.) of ash present. The bark when shaken up with water yields a frothy solution, which is neutral in reaction, and is used in cleaning cloth when it is important to preserve the original colours. The emulsifying substance is *saponin* (a collective name for a group of glucosides), which is not toxic, but is accompanied by two poisons, sapotoxin and quillajic acid. Saponin is widely distributed in flowering plants, and is usually associated with toxic substances. Its presence is familiar in a number of caryophyllaceous plants belonging to the genera *Saponaria, Gypsophila, Dianthus, Lychnis, Silene,* and others, whose underground parts are known as 'soap-roots.' The ordinary (red) soap-root is composed of underground stems and roots of the soap-wort, *Saponaria officinalis* (Linn.); the (white) soap-root of Hungary, Mediterranean countries, the Levant, and the East, is composed of the peeled roots of various species of *Gypsophila*.

SOAPSTONE *v.* TALC.

SOAP-WORT. *Saponaria officinalis v.* SOAP-BARK.

SOBREROL *v.* TERPENES.

SOD OIL *v.* DÉGRAS.

SODA (NATIVE) *v.* NATRON ; TRONA.

SODALITE. A rock-forming mineral of the composition $Na_4(AlCl)Al_2(SiO_4)_3$ and crystallising in the cubic system. Other members of this group of minerals are mentioned in the article LAPIS-LAZULI. It is white, grey, or bright blue in colour; sp.gr. 2·3; and occurs as a constituent of the igneous rock sodalite-syenite. At Litchfield in Maine, on the Ice River in Kootenay Co., British Columbia, and at Bancroft in Hastings Co., Ontario, large masses of sky blue to deep blue sodalite are found. At Bancroft it has been quarried in some quantity for use as an ornamental stone under the trade-names 'Princess Blue' and 'Alomite.' The material takes a good polish, and has somewhat the appearance of marble, but it is considerably harder (H.=5½) than this. L. J. S.

SODA-NITRE *v.* NITRATINE.